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ST. CLAIR RIVER POLLUTION INVESTIGATION (SARNIA AREA)

January 28, 1986

The Honourable Tom McMillan, P.C., M.P.,
Minister of Environment
Government of Canada

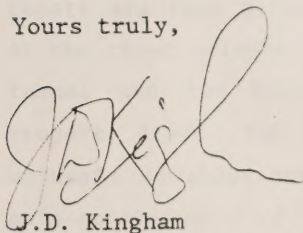
The Honourable James Bradley, M.P.P.,
Minister of Environment
Government of the Province of Ontario

Gentlemen:

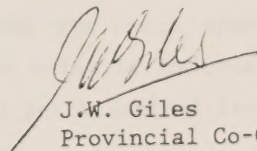
We are pleased to forward for your consideration, the report of the St. Clair River Pollution Investigation. The investigation was undertaken at your request during the period September 1st to December 31st, 1985, under the auspices of the Review Board of the Canada-Ontario Agreement Respecting Great Lakes Water Quality.

Thank you for your consideration.

Yours truly,



J.D. Kingham
Federal Co-Chairman



J.W. Giles
Provincial Co-Chairman

PREFACE

The Canada-Ontario Report on the "St. Clair River Pollution Investigation (Sarnia Area)" places emphasis on the assessment of technical information collected by the two parties in the September-December 1985 period, following the perchloroethylene spill to the St. Clair River by Dow Chemical Canada Inc., in August 1985.

The discovery in 1984 and 1985 of "black tarry" substances overlying the nearshore sediments in the Dow/Polysar area, combined with knowledge of the perchloroethylene spill and the associated appearance of other significant chemical compounds, to a large extent dictated the area of the subsequent investigations and the contaminants analyzed.

The major technical findings and interpretations in this report are thus generally restricted to an eight-kilometre reach of the river between a point two kilometres north of the CN Rail tunnel and two kilometres south of the Suncor Sunoco Group property line. The chemicals examined are trace organics, with emphasis on chlorinated organics and volatile hydrocarbons, the main constituents of the refinery and petrochemical industries in that area.

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1. GLOSSARY AND TERMS

HCB	-	Hexachlorobenzene	
HCBd	-	Hexachlorobutadiene	
HCE	-	Hexachloroethane	
OCS	-	Octachlorostyrene	
QCB	-	Pentachlorobenzene	
TCB	-	Trichlorobenzene	
TeCB	-	Tetrachlorobenzene	
PAHs	-	Polynuclear aromatic hydrocarbons	
perc	-	Perchloroethylene	
CTC or ccl_4	-	Carbon tetrachloride	
2,3,7,8-TCDD	-	2,3,7,8 - Tetrachlorodibenzo-p-dioxin	
PCBs	-	Polychlorinated biphenyls	
2,4-D	-	2,4 - Dichlorophenoxyacetic acid	
2,4,5-T	-	2,4,5 - Trichlorophenoxyacetic acid	
LC-50	-	Concentration causing 50% lethality	
EC-50	-	Concentration causing 50% of monitored effect	
WPCP	-	Water Pollution Control Plant	
ppm	-	parts per million	} equivalent
$\mu\text{g/g}, \mu\text{g.g}^{-1}$	-	micrograms per gram	
$\text{mg/L}, \text{mg.L}^{-1}$	-	milligrams per litre	
ppb	-	parts per billion	} equivalent
$\text{ng/g}, \text{ng.g}^{-1}$	-	nanograms per gram	
$\mu\text{g/L}, \mu\text{g.L}^{-1}$	-	micrograms per litre	
ppt	-	parts per trillion	} equivalent
$\text{pg/g}, \text{pg.g}^{-1}$	-	picograms per gram	
$\text{ng/L}, \text{ng.L}^{-1}$	-	nanograms per litre	
ppq	-	parts per quadrillion	

ST. CLAIR RIVER POLLUTION INVESTIGATION

2. INTRODUCTION AND EXECUTIVE SUMMARY

On August 13 to 16, 1985, Dow Chemical Canada Inc., Sarnia, Ontario, experienced mechanical valve problems, causing a spill of approximately 9400 gal (42 300 L) of perchloroethylene, a toxic dry cleaning solvent of which approximately 2500 gal (11 000 L) reached the St. Clair River. Approximately two thousand gallons were immediately recovered by DOW. This spill, combined with the discovery in 1984 and 1985 of a black tarry substance in the river overlying the sediment, led the Ministers of the federal Department of the Environment (DOE) and the Ontario Ministry of the Environment (MOE) to initiate an investigation into the nature and extent of contamination in the St. Clair River and the sources of this contamination. This investigation was carried out under the auspices of the Canada-Ontario Agreement Respecting Great Lakes Water Quality.

Background

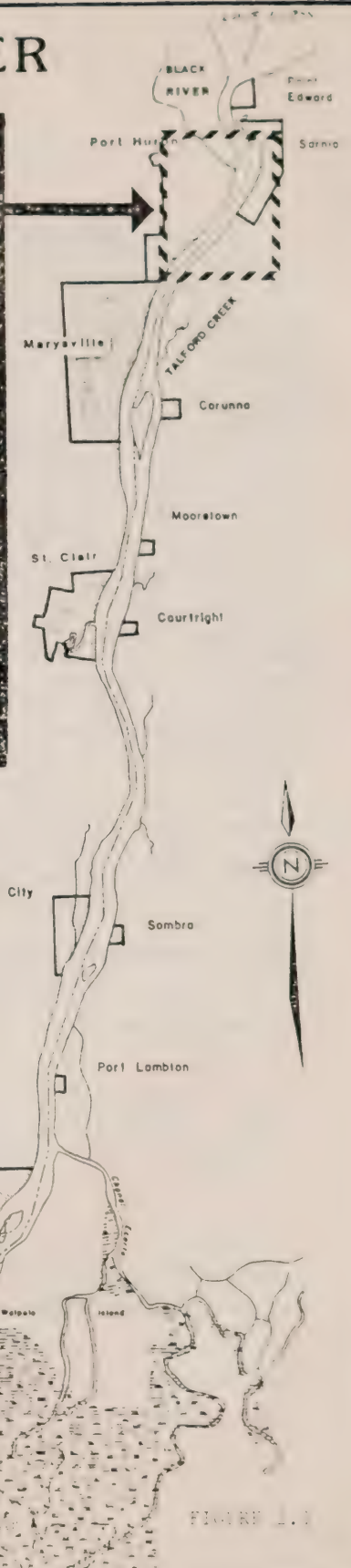
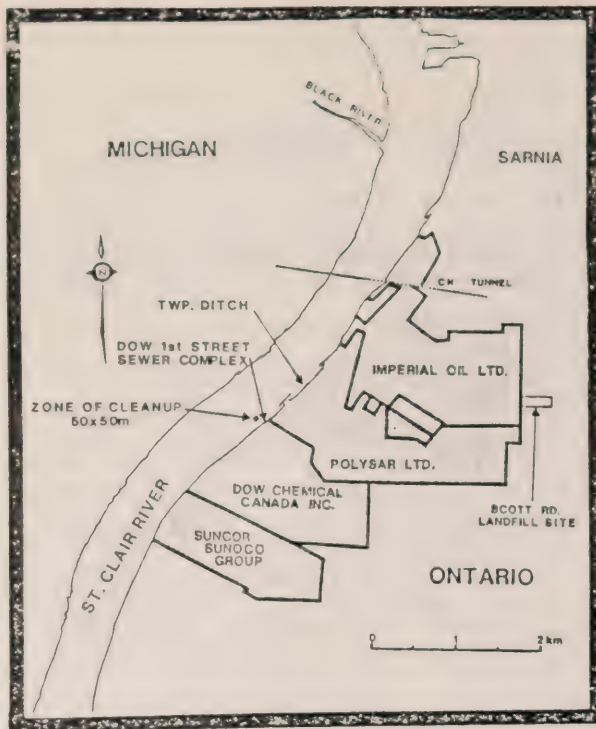
The St. Clair River flows from Lake Huron in the north to Lake St. Clair in the south, a distance of about 64 km. A map of the river and its immediate surrounding area is given in Figure 2.1.

The daily flow of the river varies from 390 million cubic meters in the summer to 490 million cubic meters during runoff. Generally, the bottom profile is consistent with a deep central channel and shallow shelves close to the shore. Most of the flow (90%) occurs in the main channel, with the remaining flow divided along each shore (5%).

The St. Clair River is an important international waterway which is subject to extensive use as a major shipping channel and as receiving water for numerous industrial and municipal effluents. This is particularly evident on the upper river along the Canadian shoreline where there are eighteen dischargers including 6 municipal sewage treatment plants and 12 industrial waste dischargers. Approximately 1.7 billion litres of industrial effluent and cooling water is discharged to the river daily from the large petrochemical complex on the Canadian side. Municipal water intakes from the St. Clair River provide treated drinking water to several American and Canadian communities. The river is also a source of water for numerous industries, including once-through cooling water for electric power generating plants.

The river is used extensively for sport fishing and provides spawning grounds for over 20 fish species. In 1980 Canadian sport fishermen took home an estimated catch of 152 000 fish. The U.S. shore contains many recreation facilities, including campgrounds, marinas and a state park while in Canada, the St. Clair Parkway Commission oversees 19 parks in total approximately 500 acres (250 ha.).

ST. CLAIR RIVER



LAKE ST. CLAIR

FIGURE 1.1

Scope and Context of the Study

This investigation was carried out in response to the discovery of the tarry globules and preliminary to a larger, more in-depth Canada-U.S. scientific investigation of the Detroit, St. Clair and St. Mary's rivers. That study, the Upper Lakes Connecting Channels Study (UGLCCS), began in 1984 and will be completed in late 1987. The major purpose of the UGLCC study is to delineate comprehensively the environmental impact of pollution sources to these rivers as a basis for the development of specific remedial action plans. These plans have been requested by the International Joint Commission under the 1978 Canada-U.S. Great Lakes Water Quality Agreement as a means of monitoring the restoration of the historically degraded areas. This current investigation serves as an immediate impetus for new and strengthened regulatory and surveillance efforts to resolve the pollution problems discussed.

Extensive survey work has been ongoing since 1977 by MOE to determine the environmental impact of chemical contamination to the river.

In order to define the extent of the contamination due to the Dow spill, MOE launched an intensive investigation of water quality and sediments in the area between Polysar and Suncor (fig. 2.1) as well as the river delta (Chenal Ecarte). Studies on biological effects, including benthic surveys and investigations into contaminant levels in young-of-the-year fish, caged clams and sport fish previously collected, as well as assessments of the toxicity of the sediments to biota, were conducted. Eight water treatment plants were also monitored for perchloroethylene on a daily basis until mid-September. Following the initiation of the clean-up by Dow in November, MOE also initiated monitoring at three drinking water plants

(Walpole, Wallaceburg and Marysville, Michigan) on a twice daily basis.

DOE also initiated intensive sediment and water surveys to define the extent of contamination in the study area. DOE and MOE, sampled industrial intakes and point source discharges in the study area. Ground-water samples were collected from piezometers inside the CNR St. Clair river tunnel, which is located upstream from Imperial Oil, and the tunnel dewatering discharge.

Samples were analyzed for volatile organics, chlorinated extractables polynuclear aromatic hydrocarbons and chlorophenols; sediment were also analyzed for dioxins. Because the point source effluent study was limited to single samples from each source, any interpretation made respecting representative contaminant concentrations and loadings is tentative. Notwithstanding the differences in sampling dates and locations and the variations in analytical methodologies, both MOE and DOE water, sediment and effluent data sets were found generally to be complementary and consistent with each other.

AMBIENT CONDITIONS

Perchloroethylene Puddles

Depressions in the river bottom in the vicinity of the Dow spill site have allowed the accumulation of chemical "puddles". These puddles were concentrated in an area approximately 50 m X 50 m, adjacent to the shoreline at the Dow 1st Street sewer complex.

In this area, the chemical composition of the puddles sampled in September, prior to the November clean-up, was mainly (97%) perchloroethylene, (perc). Analysis of puddle composition in December and January showed perchloroethylene concentrations in the order of 60% and carbon tetrachloride at 30%. These latter samples were taken from puddles found in areas from which the sediment was removed. Chlorinated organics, in all samples included hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), hexachloroethane (HCE), octachlorostyrene (OCS), pentachlorobenzene (QCB), trichlorobenzene (TCB), and tetrachlorobenzene (TeCB) and amounted to 3%. Other compounds were also found in the part per billion range, such as polynuclear aromatic hydrocarbons (PAHs), dioxins, furans and chlorophenols.

The average level of total dibenzodioxins reached 35 ppb. Tetra- and octa-chlorinated dibenzo dioxins accounted for 40% and 45% of the total dioxins, respectively. The highly toxic dioxin isomer 2,3,7,8-TCDD was not detected in the puddles. Total dibenzo-furans averaged 101 ppb. Tetra- and octa-furans formed the main congeners.

The above listed chemicals, with the exception of dioxins and furans, were also found in the dissolved phase in the discharges originating from Dow's 1st Street sewers.

A reach approximately 100 m along Dow's shoreline was found to be devoid of benthic life forms, and sediments in this section were acutely toxic to test organisms, as evidenced by laboratory toxicity studies using these sediments. The contaminated perchloroethylene puddles have had a more localized

effect around Dow's outfalls. In contrast, farther downstream, the effects of ongoing continuous discharges were predominant as evidenced by contamination of sediments with chlorinated benzenes, a minor component in the puddle composition.

Explanation of the Formation of the Perchloroethylene Puddles

A number of possible pathways were considered, to explain the presence of puddles of perchloroethylene and carbon tetrachloride contaminated with high levels of chlorinated compounds such as hexachlorobutadiene and hexachlorobenzene.

The puddles collected in September and December had significantly different concentrations of carbon tetrachloride. The most likely explanation for the puddles observed in September is that they resulted from the August perchloroethylene spill, which before reaching the river, was contaminated by residual waste materials in the sewers, drains and catch basins. Residual waste materials known to be in the river sediment may also have contributed to the contamination of the perchloroethylene puddles.

The presence of carbon tetrachloride in the puddles found in the cleaned up area in December and January suggest that these puddles are not attributable to the August perchloroethylene spill. The relatively constant ratio of perchloroethylene to carbon tetrachloride (2:1), suggests a source(s) other than the spill. Migration from contaminated areas via subsurface pathways either to the sewers or the river is a possibility. A more thorough examination of Dow's production and waste disposal practices, present and past, is warranted.

One possibility that was considered and discounted was that the contaminant puddles may have been caused by escape of wastes disposed of by Dow down deep wells into a cavern situated in the Salina salt formation, approximately 700 m below ground surface. Although wastes containing the principal chemicals identified in the puddles were disposed of by Dow into this cavern as recently as 1984, the cavern is not pressurized and therefore there is no obvious driving force which could bring these wastes back to the surface.

Clean-Up of the Puddles

Following the August perchloroethylene spill, Dow immediately initiated vacuuming the spilled material from the river near the shore. On November 14, Dow again began vacuuming of puddles and contaminated sediments in an area 50 m x 50 m adjacent to the Dow shoreline under the supervision of MOE and DOE. The vacuuming operation was completed on December 23. The recovered material is being stored in holding ponds on the Dow site. Some of the decant water has been treated and the remaining vacuumed materials will be treated in the spring. Dow has reported that approximately 2500 gal (11 000 L) of the perchloroethylene were recovered as a result of the two separate vacuuming operations. A program is currently in effect whereby Dow is continuing to vacuum residual puddles in the area after visual inspections. On January 3 Dow divers observed a few more puddles and 5 gal (22 L) of perchloroethylene were removed. On January 9, Environment Canada's remote underwater camera photographed the existence of several more puddles.

On January 13 and 15, Dow carried out underwater inspections of the outfall area and placed markers on six puddles. On January 16, MOE had an independent commercial diver inspect, describe and mark 22 puddles. Total volume of the puddles was estimated to be 10 - 15 gallons.

DOE carried out a filming inspection of the bottom on January 17 when a strong chemical odour emanating from an upstream source (being investigated) prevented Dow divers from attempting a clean-up of the remaining puddles. Dow attempted to vacuum on January 20 or 21. (Water clarity was poor on the 18th and 19th.) Ice jammed along the waterfront prevented an early start on the 20th. Dow will also place three specially-made collectors on the cleaned-up river bottom. These collectors are designed to determine whether there is seepage of materials from the river bottom. Dow will also photograph the installation process, if possible. Upon completion of this activity by Dow, MOE and DOE will carry out an intensive examination of the area using both divers and the underwater video-tape camera. Further examination, monitoring and clean-up will be continued until the incidence of puddles in the area ceases and the source is identified and controlled.

On January 22 (as this report goes to press) Dow found a very small, slow flow of dark material running under the 54-inch sluice sewer (part of the 1st Street sewer complex). This material, as analyzed by Dow, contained 77% perchloroethylene and 6% carbon tetrachloride, the two principal constituents of the puddles found in the river. This seepage was found approximately 50 to 60 feet back from the discharge point in the river at a depth of approximately 30 feet underground. Dow is presently examining the interior of the tile drain and digging a trench perpendicular to this sewer to catch the flow and

prevent it from reaching the river. Dow began excavation of these pipes in mid-January after the DOE underwater camera took extensive footage of the puddles in the cleaned up area (January 9). The film footage was made available to both MOE and Dow. This discovery appears to substantiate DOE/MOE's conclusion that the puddles being cleaned up in November and December were not a result of the August perchloroethylene spill but were the result of some small continuous leakage of contaminated material from the Dow site.

Water Quality

Bottom and surface water samples collected from the study area contained appreciable concentrations of hexachlorobenzene (HCB), hexachlorobutadiene (HCBd), hexachloroethane (HCE), octachlorostyrene (OCS), tetrachlorobenzenes (TeCB), perchloroethylene (perc), carbon tetrachloride (CTC), chloroform and other volatile chlorinated hydrocarbons. Between 10- and 100-fold increases in concentrations over upstream background levels were observed to occur in the vicinity of the Township ditch and the Dow property. The high levels persisted throughout the rest of the study area. Mean concentrations of perchloroethylene and carbon tetrachloride at various transects in the study area are presented in Figure 2.2.

The November survey results indicated significantly lower levels of volatile hydrocarbons in the study area (perchloroethylene and carbon tetrachloride) than the September survey results. Measured levels met published ambient water quality criteria for the protection of aquatic life.

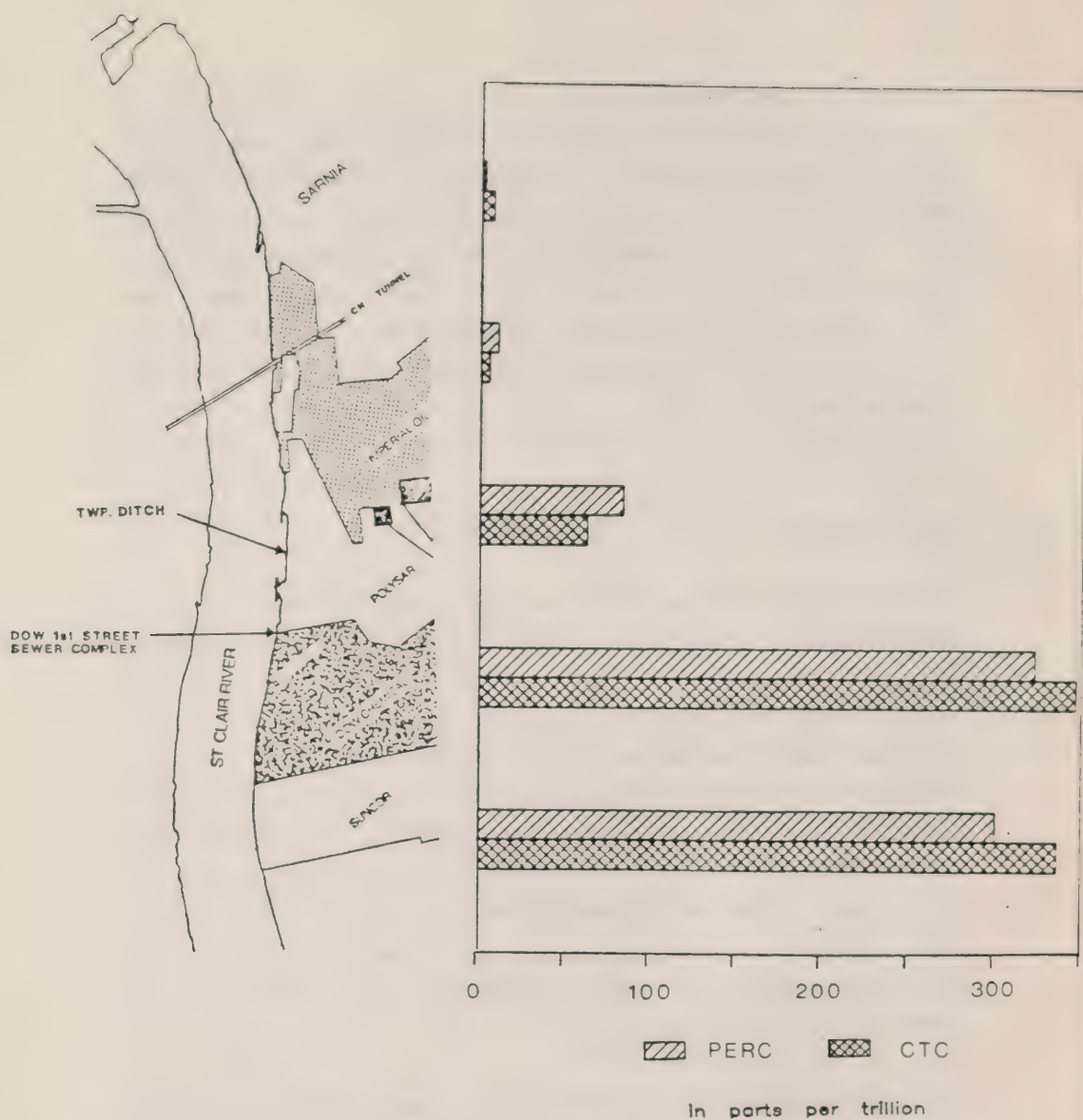


Figure 2.2 Concentrations of perchloroethylene and carbon tetrachloride in water in the Upper Reach of the St. Clair River.

Chlorinated organics analyses showed significant exceedances of provincial ambient objectives for the protection of aquatic life in the vicinity of Dow's 1st Street sewer. Based on maximum levels, the following exceedances were observed 100 m downstream from the 1st Street sewer complex: 370-fold for HCB, 13-fold for HCB_D, 5-fold for QCB, 3-fold for 1,2,4-TCB.

At a distance of 600 m downstream from Dow's 1st Street sewers, levels of HCB exceeded the objective by 100-fold. This reinforces the importance of obtaining reductions of HCB at source, considering the toxicity and persistence of this compound and the fact that it is categorized as a potential carcinogen.

The two major sources for the chlorinated organics are the Township ditch and the 1st Street sewer outfalls. During the present study, Dow's 1st Street sewers had a more pronounced adverse effect on St. Clair River water quality than the Township ditch. In 1983/84, Dow dredged the highly contaminated section of the Township ditch; the Dow Scott Road ditch was excavated and replaced with a submerged sewer.

Volatile hydrocarbons (mainly CTC, perc) as discharged from Dow's point sources resulted in high levels of these chemicals in river water. A few higher values of CTC and perc were also observed in the vicinity of the CN tunnel (upstream from the Township ditch) on both sides of the river, but the sources of these have not been identified.

Analyses of bottom waters from depressions in Chenal Ecarte confirm that there was no evidence of organics having accumulated in these holes when compared with waters just upstream.

Sediments

Contaminants which were found in elevated levels in sediments were mainly chlorinated organics and volatile hydrocarbons, both of which are attributed to discharges from refineries and petrochemical plants. In general, these contaminants were confined to a band approximately 100 m wide along the Ontario shoreline between the Township ditch and a point south of the Suncor property. Major organic contaminants were hexachlorobenzene, hexachlorobutadiene, octachlorostyrene, carbon tetrachloride, perchloroethylene and hexachloroethane. No regulatory guidelines are currently available to assess the significance of these levels;-they are being developed.

Low, but measurable concentrations of organic contaminants were also found in sediments upstream from Imperial Oil in the Sarnia industrial complex. Concentrations increased and reached maximum levels opposite Dow's 1st Street sewer outfalls. Levels in parts per million persisted to the southern end of the Suncor property. Mean concentrations of perc, CTC, HCB and HCBd at various transects along the river are shown in Figure 2.3.

The lateral distribution of chemical concentrations opposite Dow's property revealed higher levels offshore than in the near shore areas. For example, levels of HCB at 40 m offshore, opposite the 1st Street sewers, were 133 ppm compared with 6 ppm at 20 m offshore. This pattern of higher levels offshore, relative to near shore concentrations, was also observed at a location 300 m downstream from the 1st Street sewers. In addition, levels of HCB at this same location were increased by one order of magnitude, indicating effects of continuous discharges from the areas including Dow, Polysar and the Township ditch. At

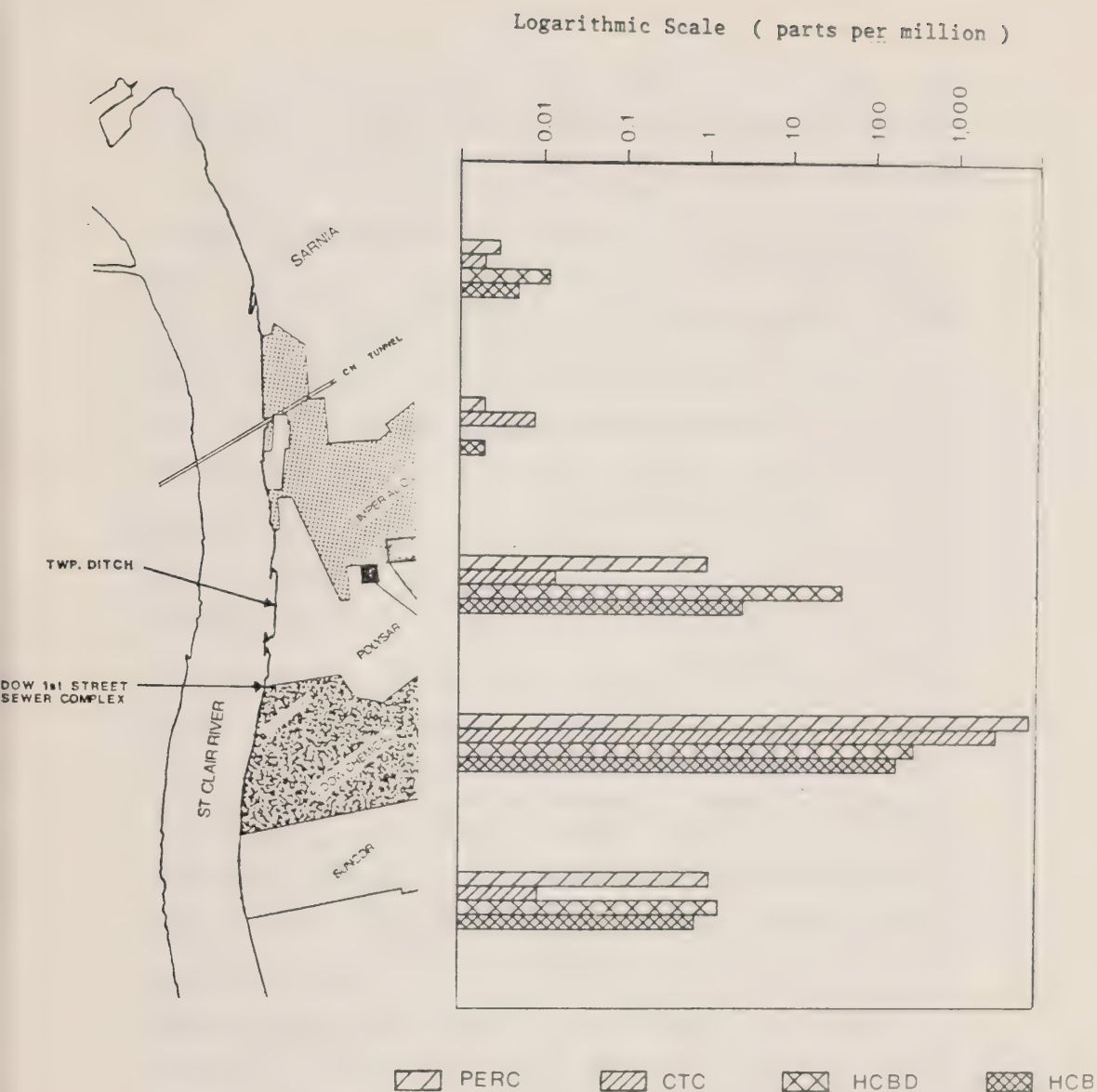


Figure 2.3 Concentrations of chemicals in sediments in the Upper Reach of the St. Clair River.

the southern end of Suncor, the lateral distribution of contaminants in sediments exhibited the usual pattern of high levels near shore compared to the offshore locations.

Dibenzodioxins and dibenzofurans found in the surficial sediments were much lower than those found in the puddles adjacent to the Dow property. A maximum level of 15 ppb total dibenzo-p-dioxins was found in sediments opposite the 1st Street sewers. Octachlorodioxin was the main congener. The maximum level of total dibenzofurans was found in sediments just above Dow's 1st Street sewers. Octachlorofurans was the main congener. At the southern end of the Suncor property, total dibenzo-p-dioxins levels decreased to 0.1 ppb and total dibenzofurans to 1 ppb. Farther downstream, levels decreased to near or below the detection limit (0.01 ppb). No 2,3,7,8-TCDD was detected in sediments.

Farther downstream, sediments in the vicinity of Walpole Island and Wallaceburg water intakes and in Lake St. Clair revealed only trace levels of some volatile hydrocarbons and chlorinated organics. No chlorinated dibenzodioxins or chlorinated dibenzofurans were detected in sediments near these water supplies. Similar findings were also noted in bottom depressions in the Chenal Ecarte.

During the sediment surveys core sampling along the Ontario shore revealed two distinct groups of sediment contamination. One group, which includes hexachlorobenzene, hexachlorobutadiene, octachlorostyrene and pentachlorobenzene, is associated with Dow's discharges. These chlorinated organics are found mainly in the surface sediment and are considered to originate mainly from Dow Chemical, the only known producer of chlorinated solvents in the area.

The other group, which is described as tar-saturated sediments, was found in the deeper layers of the cores. The source and identity of the tar-saturated sediments are not known at present. These sediments do not extend beyond 25 m from shore.

The cohesion provided by the tars apparently stabilizes the contaminated sediments and prevents or slows their movement via bedload transport. These tar-saturated sediments are not related to the perchloroethylene puddles observed near Dow.

Biota

Benthos

The health of the macrozoobenthic communities in the St. Clair River was assessed in 1968, 1977 and 1985. The results of the 1985 survey show that the benthic community is impaired in the immediate area of the petrochemical industry. A zone of impaired water quality was confirmed along the waterfront of Polysar and a severely impaired water quality zone was identified from Dow's 1st Street sewer to just down river of Suncor. Relative to 1977, however, changes in the benthic community suggest that water quality conditions of the whole river have improved markedly (Fig. 2.4).

A comparison of water quality "zones" between 1977 and 1985 indicates that the down river zone of "good" water quality advanced upriver approximately 10 km over the eight years (Fig. 2.4). In addition, water quality conditions within the "impacted" and "recovery" zones have improved since 1977. Low densities of some pollution-intolerant benthic species that were

characteristically absent from the impacted zone in 1977 were present at most stations in the impacted zone in 1985. A general increase in species richness was also noted in the recovery zone over 1977.

These changes suggest that the abatement programs implemented over the past eight years have had a significant beneficial effect on the water quality along the Canadian side of the St. Clair River.

Young-of-the-Year Fish

Current monitoring of the young-of-the-year fish revealed that accumulation of HCB and OCS had occurred to levels of 230 and 560 ng/g, respectively, in these fish downstream from Suncor. These levels are well above those found at Lake Huron control sites. Perchloroethylene levels in fish reached 380 ng/g at the same location. At the Lambton Generating Station and Mitchell's Bay, levels of perchloroethylene up to 600 ng/g were found in the juvenile emerald shiners.

Dioxin residues were low in the young fish and no tetra congeners were found. The dibenzofuran residues were of some concern, especially as tetra congeners were dominant and reached levels of 1300 pg/g at Suncor. Fish at the river headwater had 1200 pg/g. Isomer specific data are not available.

Caged Clams

Analyses of caged clams placed in the river at locations from Lake Huron to Port Lambton indicated that chlorinated organics were accumulated to a significant degree in the clams placed in the vicinity of industrial point sources. The area where the significant accumulations took place extended from the Polysar/Dow property line to the southern end of Suncor. Maximum uptake was observed to occur opposite the 1st Street sewers of Dow. Accumulation was discernible as far downstream as Port Lambton.

Sport Fish

The most recent data available (1983) for HCB in Lake St. Clair sport fish (edible portion) show that levels of this contaminant have declined since 1981. Levels in carp are 10 ppb, and channel catfish have residues of approximately 40 ppb. The 1983 data for OCS are 40 ppb and 90 ppb for carp and channel catfish, respectively. Residues of HCB and OCS in channel catfish are higher in Lake St. Clair than those in Lake Huron. For carp, the reverse applies. No consumption guidelines have been established for these compounds. Mercury levels in the edible portion (skinless, boneless fillet) exhibited a significant decline during the period 1970 to 1985. The current average level is about 20% to 30% of the 1970 value. Similarly, PCB levels have also declined compared with values in the mid-1970's. Two species of fish collected in 1982 from Lake St. Clair contained 2,3,7,8-TCDD. Mean levels were 0.6 ppt for carp, 0.89 ppt for channel catfish, whereas no 2,3,7,8-TCDD was found in walleye. These levels are all below the National Health and Welfare guideline of 20 ppt.

Acute Lethality

Sediments collected in September just below the Dow 1st Street sewer outfall were acutely toxic to three species of test organism in a laboratory test situation. The sediments collected from the "chemical valley" upstream from Dow were also acutely lethal to some organisms, whereas control sediments collected upstream above the "chemical valley" were non-lethal. Sediments collected in November below Dow were not as acutely lethal to the test organisms, although some organisms were still killed during 96 hours of exposure.

Treated Drinking Water

Water supplies at communities along the St. Clair River were intensely monitored following the Dow spill. Most organics could not be detected and the few that were observed, did not pose a threat to drinking water supplies downstream. Eight water treatment plants were monitored for perchloroethylene on a daily basis from the end of August until the end of September. During this period of monitoring, the highest level of perchloroethylene detected in treated water was 4 $\mu\text{g/L}$ (ppb). The World Health Organization's (WHO) tentative guideline is 10 ppb for a lifetime (70 years) consumption of drinking water. Continued monitoring showed a decline in approximately two weeks to below the detection limit (1 $\mu\text{g/L}$). Monitoring during the Dow spill clean-up showed that levels did not exceed the detection limit.

No dibenzo-p-dioxin or dibenzofurans were detected in any samples of treated water. 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, pentachlorobenzene, benzene, carbon

tetrachloride and hexachlorobutadiene found in the St. Clair River water were detected on isolated occasions in treated waters at levels below the WHO and EPA criteria for drinking water. Raw and treated drinking water from eight plants was monitored on a weekly basis for 139 chemicals of concern.

SOURCES OF CONTAMINANTS

Point Source Effluent Survey Conclusions

These conclusions are based on the point source effluent study undertaken by DOE, in cooperation with MOE, at the end of November 1985. This study was limited to single samples from each source. Dow Chemical effluents, especially from the 1st Street sewers, contain many of the same compounds found in the perchloroethylene puddles. The continuous discharge of contaminated effluents from the Dow 1st Street sewers does not in itself account for the formation of the perchloroethylene puddles. Compared with the other point sources sampled, Dow was the major source of neutral extractable chlorinated organics, especially 1,2,4-trichlorobenzene, hexachlorobenzene, hexachloroethane and hexachlorobutadiene. (For other possible sources, see page 8.)

The Dow sewers are significant sources of volatile pollutants compared with other industrial sources in the present survey and those studied previously on the Great Lakes. The total net loading for volatile hydrocarbons was estimated to be 242 kg/d. Six major pollutants accounted for 84% of this loading (1,2-dichloroethane, perchloroethylene, 1,2-dichloropropane, carbon tetrachloride, benzene and ethyl benzene). Ethyl benzene and benzene totalled 132 kg/d.

For the Esso Petroleum, Esso Chemical and Sarnia WPCP effluents, the contaminants analysed were generally found at very low concentrations requiring zero or minimal dilutions to achieve ambient water quality standards and objectives. The total net loadings of volatile hydrocarbons from these three sources were 0.96 kg/d, 2.6 kg/d and 2.0 kg/d, respectively.

Polysar was a major source of benzene, which originated mainly from the 72-inch sewer. The total net loading of volatile hydrocarbons was 115 kg/d, of which 112 kg/d was benzene.

The Suncor intake, located downstream from Dow Chemical, contains many of the compounds being discharged at high concentrations by Dow and Polysar. The total net loading of volatile priority pollutants from Suncor was 1.1 kg/d.

A comparison of historical organics data for 1979/80 with the present survey indicates some improvements, but a greater number of samples would be required to make a proper comparison coupled with an examination of abatement measures that have occurred during the period.

The Dow Scott Road landfill leachate contained the chlorophenoxy herbicides 2,4-D (18 µg/L) and 2,4,5-T (1 µg/L), high concentrations of volatile organics including 1,1-dichloroethane, 1,2-dichloroethane, chloroform, trichloroethane and 1,1,2-trichloroethane. Loadings could not be calculated due to a lack of flow information.

The levels of 2,4-D and 2,4,5-T in the disposal site leachate appeared to be unaffected by carbon treatment. High concentrations of volatiles were also observed after carbon

treatment. All chlorophenols were effectively removed by treatment. The Scott Road site was also a source of trichlorobenzene and hexachlorobutadiene. The Dow 1st Street 30-inch acid tile and the Polysar 66-inch sewer also contained detectable levels of 2,4-D.

The Scott Road outfall contained many of the contaminants discharged by the Dow Scott Road landfill, although, there may be other sources of chlorinated organics, especially chlorinated benzenes, to the Scott Road ditch.

The Township ditch water at a point upstream from Polysar was moderately contaminated with volatile organics and extractable chlorinated compounds, specifically chloroform; 1,2-dichloroethane; 1,4-dichlorobenzene; 1,2,4-trichlorobenzene; and hexachlorobutadiene. The loading of volatile hydrocarbons from the ditch was similar to that of Polysar. In terms of the loading of chlorinated extractable pollutants, the Township ditch a significant source of HCBd and trichlorobenzenes.

The Township ditch sediment collected upstream from Polysar is contaminated with chlorinated benzenes, hexachlorobutadiene, octachlorostyrene (found at low levels in most of the samples) and chlorophenols.

Urban runoff in the Sarnia area was a minor source of perchloroethylene, hexachloroethane, hexachlorobutadiene, pentachlorobenzene, hexachlorobenzene and octachlorostyrene.

Possible Underground Sources

During the course of the clean-up of the perchloroethylene spill from the bottom of the St. Clair River, the possibility was raised that a hydrogeological source of contaminants existed. This was based on the fact that large quantities of industrial wastes were disposed of by deep well injection from 1958 to 1976 in the St. Clair River area. The St. Clair River Situation Report released by MOE and DOE on November 18, 1985, provides a description of these disposal practices. To date, there is no substantiated information that deep well disposal of industrial wastes is a source of the perchloroethylene puddles.

MOE and DOE undertook a study on the CN Rail Tunnel which indicated the following.

Ground-water leakage into the tunnel is around 4000 gal/day and occurs for the most part, in a 160-m section on the Canadian side of the river. Water samples were collected from the discharge sump and three piezometers located in the tunnel.

Detectable levels of chlorides, phenols and polyaromatic hydrocarbons (PAHs) were found in the water samples from the piezometers. These results suggest that industrial wastes may be contaminating the ground water around the CN tunnel on the Canadian side. Chlorinated hydrocarbons such as hexachlorobutadiene and octachlorostyrene were found at trace levels in the water leaking into the tunnel that was collected in the sump.

Upon review of existing information, hydrogeological experts unanimously agreed on the need for further specific studies before definitive conclusions regarding the occurrence of

pollution from underground sources could be made. These are listed in the Recommendations. Further, the experts concluded that the hydrogeological studies currently underway or planned under the Upper Lakes Connecting Channels Study will greatly assist in providing the information required to make more definitive conclusions.

Spills

There were 32 reported spill incidents from 1974 to date in which 10 or more metric tons of materials were discharged to the St. Clair River.

In view of the frequency and potential significance of spills into the St. Clair River, MOE is undertaking a critical review of spill control capabilities at each of the industries in the area.

CURRENT ACTIONS UNDERWAY

Spills

The need for upgrading of spill prevention, detection and response measures has been impressed on area industries. Effective 24-hour response by MOE has also been implemented through the recently established Spills Action Centre, and investigations of spill contingency measures will be conducted. Staffing of the Sarnia District Office of MOE has been expanded to ensure thorough investigation of spill incidents to support prosecutions where warranted.

Priority for Objectives

DOE and MOE have commenced a program to examine volatile compounds identified in discharges to the St. Clair River for the purposes of formulating acceptable ambient water quality objectives.

Effluent Monitoring

Each industry discharging to the St. Clair River has been assessed to identify specific chemical compounds of potential concern. The Ministry of the Environment is drafting a regulation which will require that the industries and municipalities discharging to the St. Clair River conduct comprehensive monitoring programs for listed parameters to characterize effluent quality and to provide a long-term data base for loading assessment. This monitoring program will be audited by MOE.

Point Source Control

Existing information on sediments, water quality, biota and point sources, together with experience gained from the effluent monitoring regulation (mentioned above), will be used to develop a control regulation for the industries and municipalities discharging to the St. Clair River. Through this control regulation, the Ministry of the Environment, with the scientific and technical support of DOE, will establish effluent concentrations and loading levels for all parameters which, if exceeded, will trigger additional monitoring, remedial measures, abatement and prosecution.

Source Identification of Dioxin and Furans

A sampling and analysis survey is in progress to focus on all possible sources of dioxins and furans discharging into the upper St. Clair River. Sampling includes water and sediment in sewers and drainage pathways.

Drinking Water Monitoring

A province-wide drinking water surveillance program was instituted mid-1985 by the MOE. The program routinely studies 109 compounds and includes the water treatment plants supplying Sarnia, Walpole Island, Wallaceburg, Mitchell's Bay, Stoney Point, Windsor and Amherstburg. As a result of the August 1985 spill of perchloroethylene, several St. Clair River area water treatment plants were monitored daily for perchloroethylene.

Additionally, the dioxin monitoring program was intensified following the finding of dioxins in the oily material from the river bottom. Water sampling for perchloroethylene was carried out downstream from the Dow spill clean-up activity to monitor for movement of contaminants downstream and any possible impact on drinking water supplies.

Upper Great Lakes Connecting Channels Study

In many cases, the thrust of the recommendations contained in the following section is ongoing in the UGLCCS. The projects being undertaken by agencies participating in the study are, however, more general in that they address the problems of a broader range of contaminants in a larger system. For example, the fate and pathways of many contaminants in the Detroit and

St. Clair rivers will be investigated. Those specific contaminants were selected to be studied either by their ability to represent a whole class of contaminants or by their identification as historically persistent pollutants. The recommendations presented in this report are, on the other hand, more specific to a localized event. Nonetheless, certain recommendations will be subsumed by the ongoing projects of the UGLCCS and the development of regulations for effluent monitoring and control being undertaken by the province.

Source Identification of the Contaminant Puddles

Dow Chemical initiated a number of activities on its site in mid-January specifically aimed at finding the source of the puddles in order to control it. These activities monitored by MOE and DOE include the following:

- inspection of their solvent production process to ensure that leakage of effluents and process upsets in the solvent plant are not entering the sewer complex but directed to holding ponds;
- excavation under each of the 1st Street sewers to determine if there is contaminated perchloroethylene present that could leak into the St. Clair River;
- further examination of hydrogeological characteristics of their property;
- a river sediment survey upstream of the 50 x 50 m clean-up area;
- an extensive outfall and in-plant sampling program focussed on point sources;
- further testing of effluents to characterize the behaviour of perchloroethylene in effluents;
- an engineering study of the 1st Street sewer system.

RECOMMENDATIONS

General

1. The sediment, water, point source and biota findings of the current study should be reviewed by the Technical Work Groups of the Upper Great Lakes Connecting Channels Study (UGLCCS) in the February 1986 workshop with a view to amending and augmenting the UGLCCS workplan where warranted.
2. Government and industries should accelerate investigations of available technologies and systems for maximizing control over the discharge of toxic substances to the St. Clair River. These investigations should address the specific provisions of Article VI and Annexes 8, 10 and 12 of the Great Lakes Water Quality Agreement, and should lead to the establishment of quantitative discharge limits for each contaminant of concern, based on "achievable technology" and any further stringency imposed by receiving water quality considerations.
3. Ambient water quality objectives for the volatile and chlorinated organic compounds in the St. Clair River should be established as a matter of priority.
4. Better definition of the fate and pathways of contaminants in the St. Clair River ecosystem, with particular emphasis on carbon tetrachloride, perchloroethylene, hexachlorobenzene and hexachlorobutadiene, is urgently required.

Ambient

1. Identity and probable sources of sediment contamination that persist in the deeper layers of cores collected in the vicinity of the Ontario shoreline of the river should be investigated.
2. Sources of volatile hydrocarbons particularly carbon tetrachloride and perchloroethylene, in the study area should be investigated and reduced.
3. The apparent increase in concentration of hexachlorobenzene in sediments between the CN tunnel and the Township ditch on the Ontario side should be investigated.
4. The apparent increase in the concentration of hexachlorobenzene in sediments in the vicinity of the CN tunnel on the Michigan side should be investigated.
5. Sources of the carbon tetrachloride and perchloroethylene in water upstream from the CN tunnel should be identified.
6. The presence of high concentrations of mercury in sediments opposite Dow property should be investigated.
7. Sources of hexachlorobenzene, octachlorostyrene, pentachlorobenzene and PCBs in the area between Talford Creek (Shell Canada) and Petrosar should be identified and action initiated to reduce or eliminate these compounds.
8. The drinking water surveillance program should be continued at water treatment plants on the St. Clair River.

9. Ontario drinking water criteria and objectives should be developed for 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, pentachlorobenzene, benzene and carbon tetrachloride, all of which have been found in the St. Clair treated drinking water.
10. Contingency drinking water treatment technology should be developed for use after chemical spills, i.e., mobile treatment units.
11. Additional efforts in analytical development should be undertaken to allow more precise analyses of polychlorinated aromatic hydrocarbon and polychlorinated dibenzofurans in young-of-the-year spottail shiners.
12. Additional species of sport fish from Lake St. Clair and Lake Huron (control) should be analyzed for chlorinated benzenes, furans, polyaromatic hydrocarbons and substituted phenols. This is a critical requirement, given the importance of the recreational fishery and the high public utilization of fish from Lake St. Clair.

Sources

1. The effluent levels of volatile organics, particularly perchloroethylene and carbon tetrachloride from Dow, should be reduced.
2. Based on the findings of water and sediments, Dow effluent levels of persistent chlorinated organics, notably hexachlorobutadiene and hexachlorobenzene, should be reduced.

3. The effectiveness of the Dow Scott Road landfill carbon treatment facility should be investigated. Modifications should be implemented to reduce losses of persistent chlorinated organics, especially hexachlorobenzene and hexachlorobutadiene.
4. Additional sources of chlorinated organics to the Scott Road outfall, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene in particular, should be investigated.
5. Sources of chlorinated organics to the Township ditch, in addition to those coming from the Scott Road outfall, should be investigated.
6. The source of benzene in the Polysar 72-inch sewer and of ethylbenzene and benzene in Dow's sewers should be identified and treated.
7. Volatile hydrocarbons in all sources in the Chemical Valley, particularly carbon tetrachloride and perchloroethylene, should be reduced.
8. To ascertain the extent of possible ground-water contamination in the Sarnia area, studies are required to
 - (i) Define the ground-water flow pattern in the freshwater aquifer.
 - (ii) Assess water quality in the fresh water aquifer and seepage discharge to the St. Clair River.

- (iii) Determine the hydraulic head relationships between the freshwater aquifer, the rock layers above the Detroit River Group, the deep well disposal zone and the caverns in the Salina formation.

3. AMBIENT CONDITIONS

Introduction

The discovery of puddles of black liquid on the bottom of the St. Clair River at Sarnia in 1984 and in the summer of 1985, as well as the reported perchloroethylene spill by Dow Chemical Company, have led to questions concerning the extent of contamination of the river and the safety of drinking water supplies drawn from it. Of major concern is the 8-km reach of the St. Clair River immediately south of Sarnia. This chemical valley is the home of a number of petroleum and chemical industries, mostly adjacent to the river, and which collectively discharge in the order of 1.7 billion litres of process, cooling and storm water daily. Most of these discharges take place in the near shore area where mixing is limited. For details concerning the chemicals produced and waste disposal practices in the valley, the reader is referred to "Pollution of the St. Clair River (Sarnia Area)," a situation report prepared by Environment Canada and the Ontario Ministry of the Environment (MOE) in November 1985.

Description of Study Area

The St. Clair River is approximately 63 km long with a total fall of 1.5 m. The river has three distinct reaches with different hydraulic characteristics:

- The steep upper reach between Lake Huron and the mouth of the Black River is only 5 km long and falls approximately 0.3 m in a relatively narrow and deep channel. The

channel is 450 m wide and 9 m deep. Mean surface current is 1.5 m/s.

- The middle reach extends downstream to the river delta and covers approximately 40 km. The reach width varies from 600 to 900 m and its depth varies from 8 to 15 m. Mean surface current is 1 m/s.
- The extensive delta region known as the St. Clair Flats forms the lower reach of the St. Clair River and extends downstream from the remaining 18 km to Lake St. Clair. The region is divided into several channels with mild slopes. Mean velocity is 0.7 m/s.

The river flow produces an average discharge of about 5100 m³/s, which varies seasonally from a winter low of 4200 m³/s to a summer high of 5500 m³/s.

The reach of the St. Clair River along Sarnia's industrial shoreline is a stable channel, 500 to 800 m wide and 9 to 15 m deep. The adjacent shoreline is low-lying with a height of less than 10 m and has been extensively altered by dockage, fill and shore stabilization. Most of the Canadian shore consists of concrete seawalls, sheet piling and riprap; the American shore is less developed. Comparison of early and recent aerial photographs of the area indicates that considerable artificial smoothing of the industrial shoreline by landfill occurred between 1955 and 1973.

Channel shape and depth vary down river (Fig. 3.1). North of the railway tunnel, the channel has steep, smooth sides and a

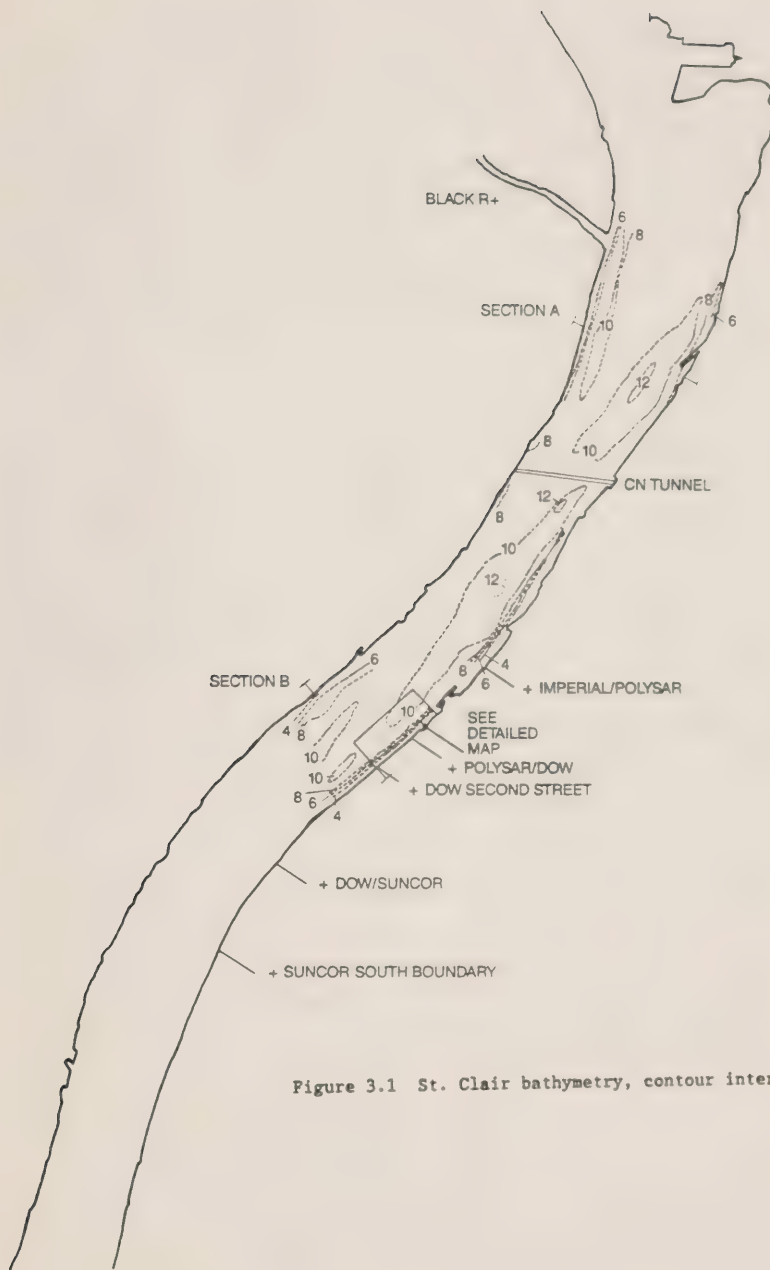


Figure 3.1 St. Clair bathymetry, contour interval 2 m.

central ridge separating Canadian and American sub-channels 2 to 4 m deep (Fig. 3.2a). The Canadian channel tends to be the deeper one. Farther south, the shape of the cross section gradually changes as the slope of the American shore decreases and the sub-channels become less prominent. This results in a shallower single channel skewed toward the Canadian shore (Fig. 3.2b). Some of the changes noted may be the result of channel deepening and maintenance dredging for navigation which has been underway since the 1890s.

The detailed morphology of the Canadian slope in the vicinity of the spill site is shown in Figures 3.2c and 3.3. The inshore slope is smooth and very steep with grades as high as 1 in 3 (18°). Bottom contours are generally parallel to the shore. The slope gradually decreases offshore from the 5-m contour, and then a pronounced break in slope, which is marked by a notch and an increase in bottom roughness, occurs between 50 and 100 m offshore at a depth of between 7 and 9 m. Local relief on this lower slope and on the adjacent channel floor ranges from 0.1 to 0.5 m.

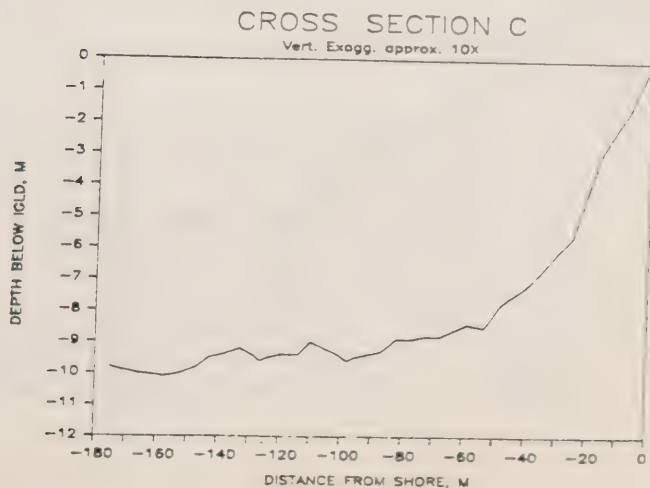
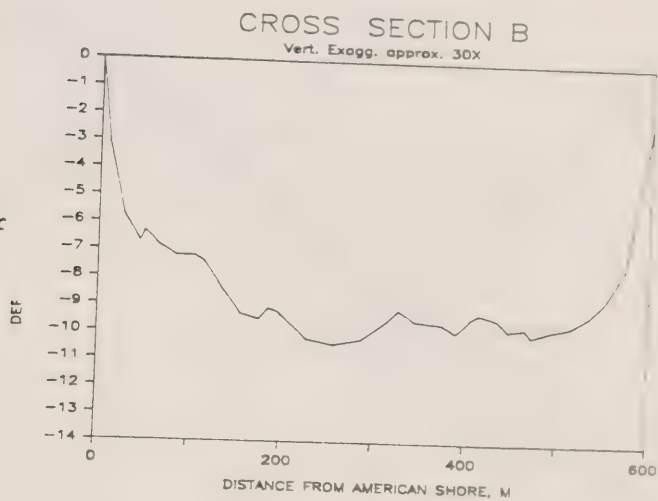
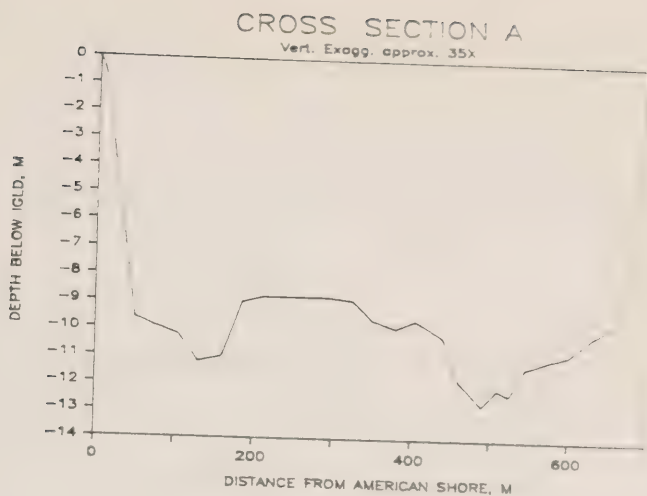


Figure 3.2 Profiles of St. Clair River bottom.

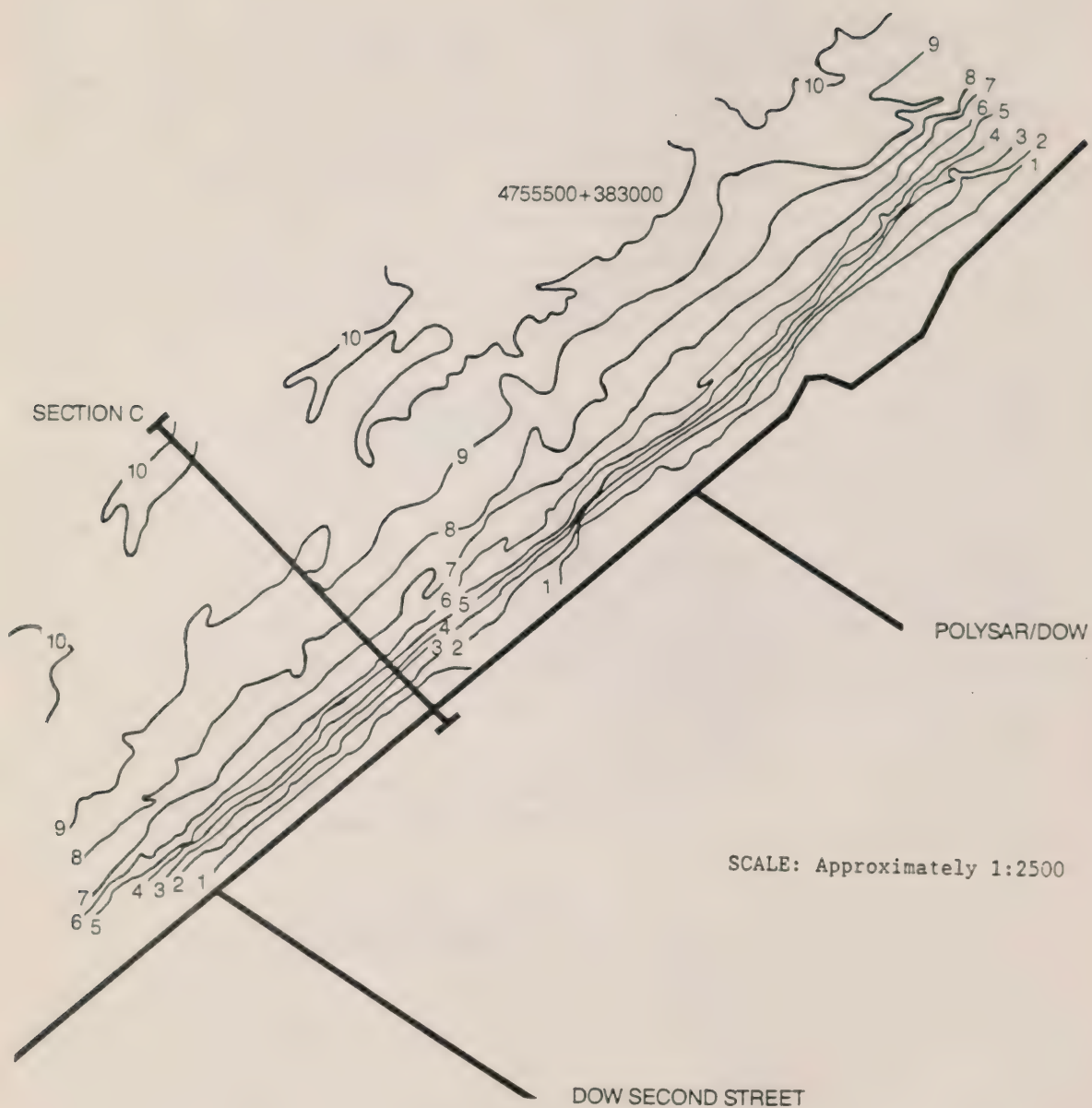


Figure 3.3 Depth contours, Dow site, 1985, contour interval 1 m.

PERCHLOROETHYLENE PUDDLE DESCRIPTION

Chemical Composition

Samples of the perchloroethylene puddles were collected by divers in September, November and December, 1985, from a site approximately 30 m offshore of the Dow Chemical 1st Street sewer complex (approximately 10 m south of the Dow/Polysar boundary). Some of these samples are from puddles which had reformed after the area had been cleaned up by Dow. Although ratios varied somewhat between samples and between laboratories, the major components in each of the six samples analyzed were perchloroethylene and carbon tetrachloride, which together accounted for over 90% of the material when analyzed by dilution and gas chromatography. The composition of a puddle from the cleaned area sampled in December is shown in Figure 3.4.

The composition of the puddle from September was similar except that the carbon tetrachloride concentration was much lower and the puddle was 97% perchloroethylene. The concentration of the minor products was consistent in all samples. Significant quantities of other chlorinated aliphatic and aromatic compounds were present as minor contaminants, making up approximately 3% of the total. Minor components for which standards were available for confirmation and quantitation included:

hexachloroethane	0.4 to 0.8%
hexachlorobutadiene	0.4 to 0.6%
hexachlorobenzene	0.4 to 0.6%
1,1,1-trichloroethane	0.5%
trichloroethylene	0.3%
octachlorostyrene	0.02%
pentachlorobenzene	0.01%
tetrachlorobenzenes	0.02%
trichlorobenzenes	0.02%

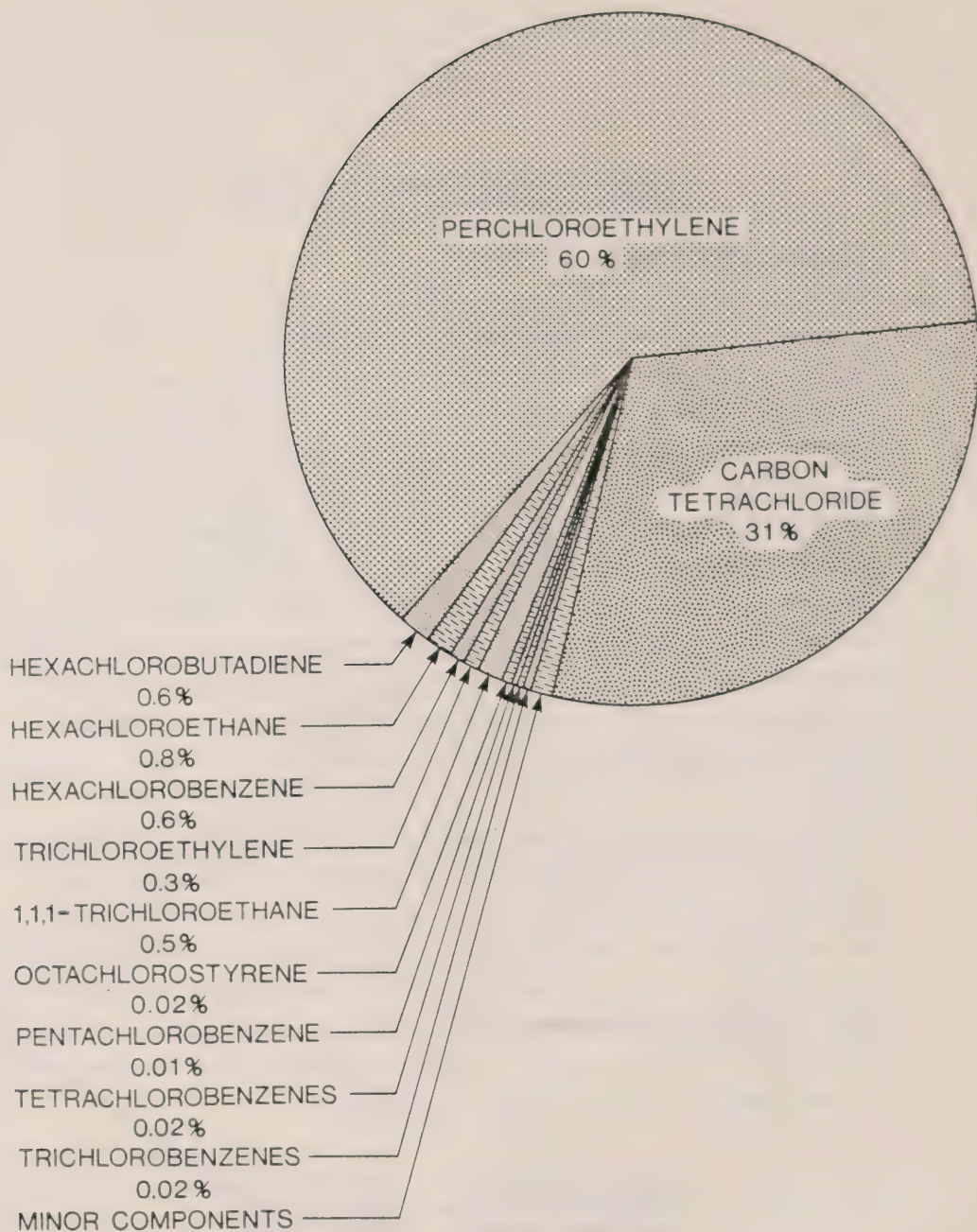


Figure 3.4 Chemical composition of perchloroethylene puddle, December 1985.

The following compounds have been identified by full-scan GC/MS but because standards are not available for many of them, concentrations were estimated from similar compounds present in the sample. The quantitations of many of these minor components for which standards are not available should be regarded as semiquantitative and their identities tentative at this time. The tentative identities and estimated concentrations of the minor components include:

tetra- and pentachloroethane	0.02%
three pentachlorobutadiene isomers	0.04%
tetra- and pentachlorobutane	0.02%
seven hexa-, hepta- and octachlorobutenes	0.08%
nona- and decachlorohexadiene	0.01%
heptachlorostyrene	0.005%
octachloronaphthalene	0.004%

Many other chlorinated compounds were present at levels less than 0.01%. For example, the following chlorophenols were detected:

2,4-dichlorophenol	3 µg/g
2,4,6-trichlorophenol	0.9 µg/g
2,4,5-trichlorophenol	0.2 µg/g
2,3,4,6-tetrachlorophenol	0.2 µg/g
pentachlorophenol	3.3 µg/g

Samples were also analyzed for chlorinated dibenzo-p-dioxins and dibenzofurans. There was no 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) detected in any of the samples at a detection limit of 0.4 ng/g. The average concentration of total chlorinated dibenzo-p-dioxins amounted to 35 ng/g with tetra- and octachloro isomers amounting to 40% and 45%, respectively. Total dibenzofuran levels averaged 101 ng/g with tetra- and octachlorinated dibenzofurans the major congeners. Tetrachloro

dibenzofurans amounted to 40% to 50% of the total dibenzofurans, while octachloro dibenzofurans ranged from 30% to 50% of the total. The 2,3,7,8-tetrachlorodibenzofuran isomer was not detected at a detection limit of 0.4 ng/g.

The 2,4-D butyl ester was found in one of the six samples at a level of 14 ppm. Since it was not detected in the other samples, this concentration cannot be considered representative. Other pesticides and herbicides such as DDT, DDE, lindane, endosulfan and 2,4-D were not detected in the puddles at a detection limit of 0.1 ppm.

Perchloroethylene Characteristics

Perchloroethylene is a colourless, nonflammable liquid used primarily as a solvent in the dry cleaning industry. It is used to a lesser extent as a degreasing solvent in the metal finishing industries (Windholz, 1976). In Canada, approximately 80% of the perchloroethylene is used in these two industries.

Perchloroethylene has a molecular formula of C_2Cl_4 and a molecular weight of 165.85. Other physical properties of perchloroethylene include a melting point of $-23.25^{\circ}C$, a density of 1.623 g/mL, a water solubility of 150 to 200 mg/L and log octanol/water partition coefficient of 2.53. The log P value indicates that perchloroethylene has a moderate affinity for lipid material and may bioaccumulate (Neely *et al.*, 1974; Neely 1979; U.S. EPA, 1979). Perchloroethylene is ubiquitous in the environment and has been found in ambient air, water, rain, food, human tissue, and various biological samples (Ofstad, 1981).

On a log scale, Figure 3.5 illustrates numerous environmental and biological responses that have been measured for perchloroethylene.

Aquatic Toxicology

The toxicity of perchloroethylene has been measured using a variety of freshwater organisms. These animals include minnows, daphnia, sport fish, and aquatic worms. The following data are representative values.

Acute Tests

<u>Organism</u>	<u>Exposure</u>	<u>Result</u>
Daphnia	48-hr EC-50	17.7 mg/L (11)
Midge	48-hr LC-50	30.8 mg/L
Fathead minnow	96-hr LC-50	18.4 mg/L
Bluegill sunfish	96-hr LC-50	12.9 mg/L
Rainbow trout	96-hr LC-50	4.8 mg/L (8)

These values indicate that perchloroethylene is moderately toxic to a variety of aquatic organisms. Alexander (1978) observed that fish surviving these tests showed loss of equilibrium, melanization, narcosis and swollen, hemorrhaging gills. The first three symptoms are indicative of perchloroethylene acting on the central nervous system of the fish. Mammalian tests frequently note this narcotic effect (Sittig, 1985). Except for those fish most severely affected, Alexander noted that the surviving fish when transferred to clean water recovered with no apparent permanent damage.

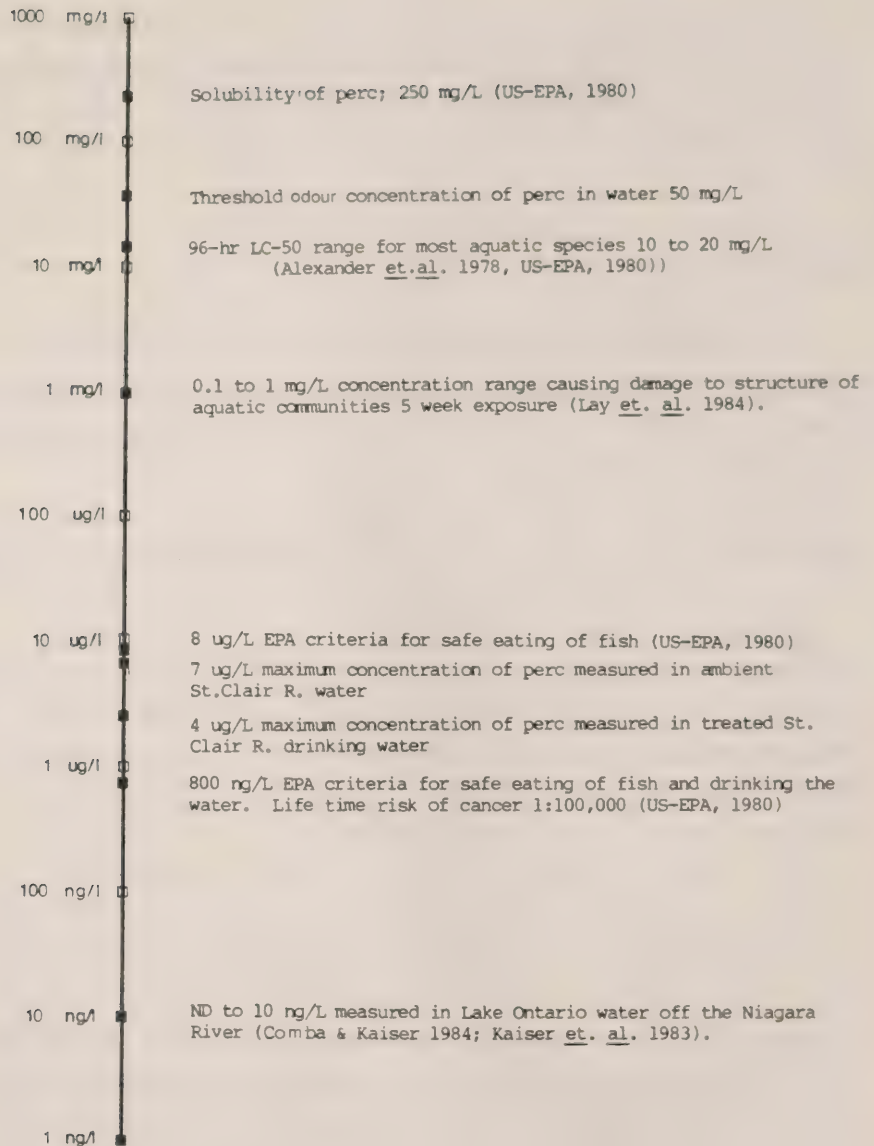


Figure 3.5 Log scale illustrating various effects of perchloroethylene in water.

Bioconcentration

The bioconcentration factor (BCF) for perchloroethylene has been measured using two fish species. For rainbow trout the BCF is 39 and for bluegill sunfish, 49. Equilibrium concentrations are reached in the fish in 21 days. When the chemical treatment is stopped, depuration is very rapid with half of the chemical being lost in less than one day (U.S. EPA, 1979). Presently, there is no evidence indicating that perchloroethylene moves up the aquatic food chain and biomagnifies.

Fate, Persistence and Movement

The major route for loss of perchloroethylene from the aquatic environment is volatilization. Laboratory studies and mathematical estimates indicate that perchloroethylene has a half-life in water of approximately 30 min (U.S. EPA, 1980), but there are no corresponding data for perchloroethylene in ambient waters. Once perchloroethylene has volatilized from the water into the air, it is subject to photo-oxidation which ultimately breaks it down. There is some evidence for microbiological decomposition, but this is probably not a major factor controlling the fate of perchloroethylene in the aquatic environment (Vogel, 1985). Perchloroethylene has a fairly low affinity for suspended and bottom sediments.

Physical Behaviour in Flowing Water

Very little is known about the physical behaviour of perchloroethylene in flowing water. Its movement and transport,

especially in the presence of bed sediments, has not been studied.

The first underwater filming of the river bottom was carried out on November 5, 1985, using the National Water Research Institute's DEEP SEA MiniROVER, a lightweight, remotely controlled, underwater video camera. On November 6, moving black puddles of liquid were observed on the river bottom at the site of the reported spill of perchloroethylene by Dow (inside the 50 m x 50 m area to be cleaned by Dow). The puddles varied in size from 2.54 cm to 30.5 cm. Their thickness was estimated to be 0.6 cm. Further film footage was obtained illustrating the unusual behaviour of these puddles (Fig. 3.6).

There is also little information on its dissolution rate while it is on a river bottom. Therefore, some exploratory tests were conducted in a laboratory flume to gain insight into the behaviour of such material in the river and to help interpret some of the behaviour observed with the underwater video camera.

The tests were conducted in a flume 1 m long and 20 cm wide. The flume walls were made of glass. Water was fed from a head tank into the flume and the downstream level was controlled with a tailgate. The water depth was maintained at approximately 10 cm for all the tests.

Two different sizes of sand with mean diameter of 1.2 mm and 0.5 mm, respectively, were used as bed material in the flume. However, essentially the same behaviour was observed regardless of which size was used.



Deep Sea MiniRover, a tethered robot mini-submarine used by the National Water Research Institute to observe river bed with a television camera.



Depth gauge and compass dials on the mini-sub are seen in foreground, with a black perchloroethylene puddle on the sediment surface



White circle marks spot on river bottom where chemical material appeared to emerge from the sediment to join larger mass seen above the circle.



Image recorded just four seconds later shows larger quantity of chemical material that has emerged or been uncovered.

Figure 3.6 Underwater Video Images

At the start of test, water was introduced into the flume and the discharge was slowly increased. A quantity of tetrachloroethylene, dyed red to make it more visible, was introduced onto the top of the sand bed by means of a hypodermic needle. It was observed that small quantities of perchloroethylene released into the flow would form small globules of up to about 3 mm in diameter. Larger quantities would form elongated puddles on the sand, similar to puddles of mercury on glass.

As discharge was increased to an average flow velocity of about 20 cm/s, the solvent globules and puddles moved downstream on top of the sand bed until they came to troughs or depressions in the sand, where they would collect and coalesce.

As the discharge was further increased, bed sediment started to move and sand waves began to form. Any perchloroethylene that was released onto the bed was swept over the crest of the sand waves and collected in the troughs. There the puddles oscillated and occasionally small globules would detach and be carried farther downstream. However, at no time did any of this material move into the sand. A most interesting phenomenon occurred when the sand waves moved downstream over the puddles. As illustrated in Figure 3.7, the advancing sand wave would gradually bury the puddle that was sitting in the trough. As most of the puddle became buried the portions of the downstream front sometimes broke off and were carried downstream. Eventually the puddle became completely buried and no evidence of it could be seen from the surface. Later the globule would reappear on the upstream face of the sand wave as it passed. It appeared at this point as if the globules were rising out of the sand when in fact the perchloroethylene had remained practically stationary while the sand wave moved by. As the solvent reappeared, globules would

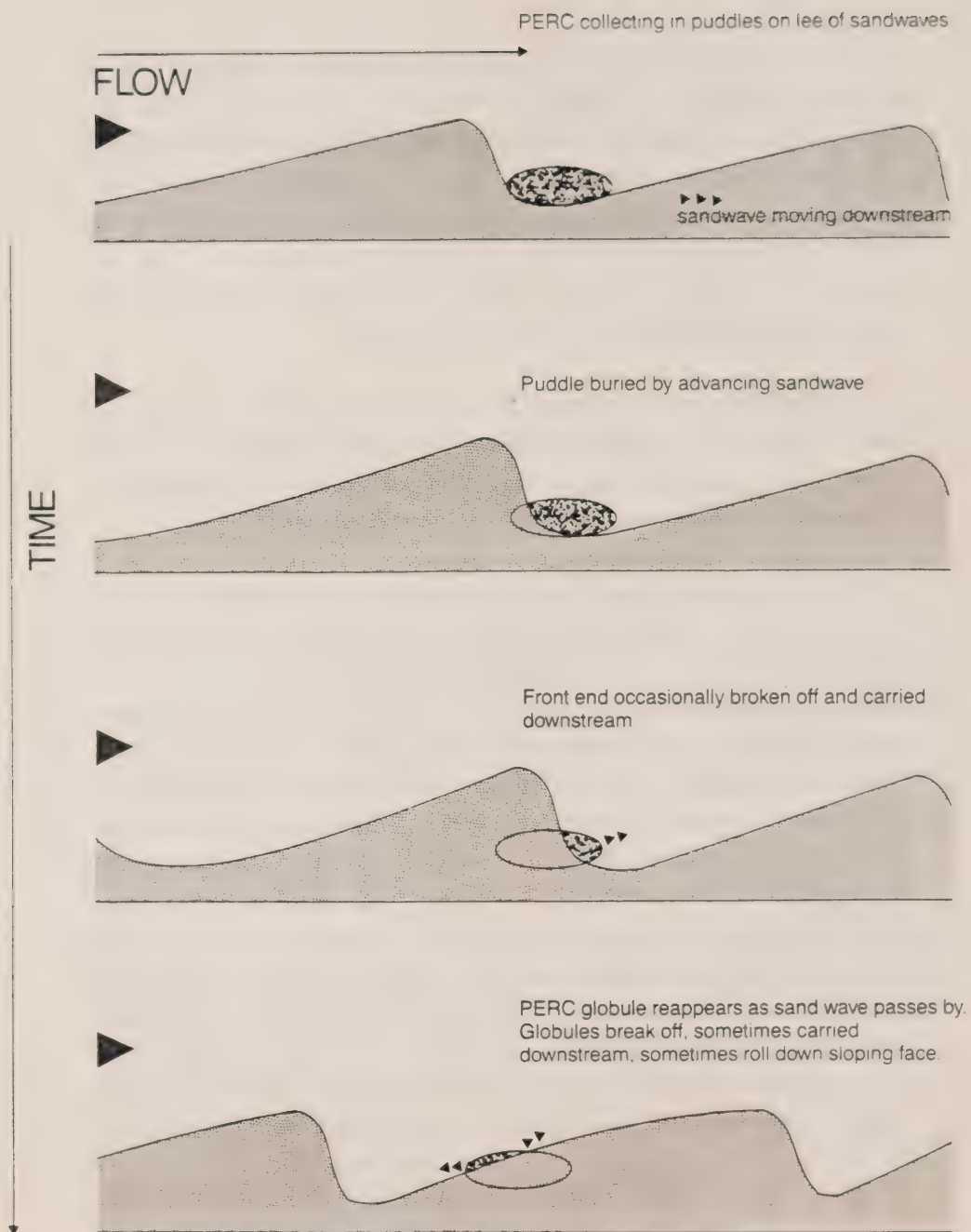


Figure 3.7 Movement of sand waves through perchloroethylene.

detach. These would be carried downstream over the crest of the sand wave or would roll down the sloping face, in the upstream direction, and stop in the trough.

These observations were made with pure perchloroethylene. Subsequent observations using the tarry material retrieved from the St. Clair River revealed the same behaviour.

Percolation through Sand Layer

A test was carried out in the flume to obtain a rough measure of the pressure head required for perchloroethylene to be forced upward through a sand layer. The bottom of the flume was fitted with a trough, 5 cm x 5 cm x 15 cm long, which was filled with sand. The top of the sand was flush with the flume bottom. Solvent was fed to the bottom of the sand layer via tubing connected to the bottom of the trough, as shown in Figure 3.8. When a certain height of the column was reached, the pressure was sufficient to force the perchloroethylene upward through the pores in the sand layer and causing it to emerge into the flume. The observations indicated that an excess pressure equivalent to about 10 cm of water was sufficient to force the perchloroethylene to move upward through the sand layer. It was also observed that it moved through the sand without disturbing or displacing it.

Dispersion from Point Sources

Material that is released in a river will disperse as it is transported downstream. To learn how chemicals that are released

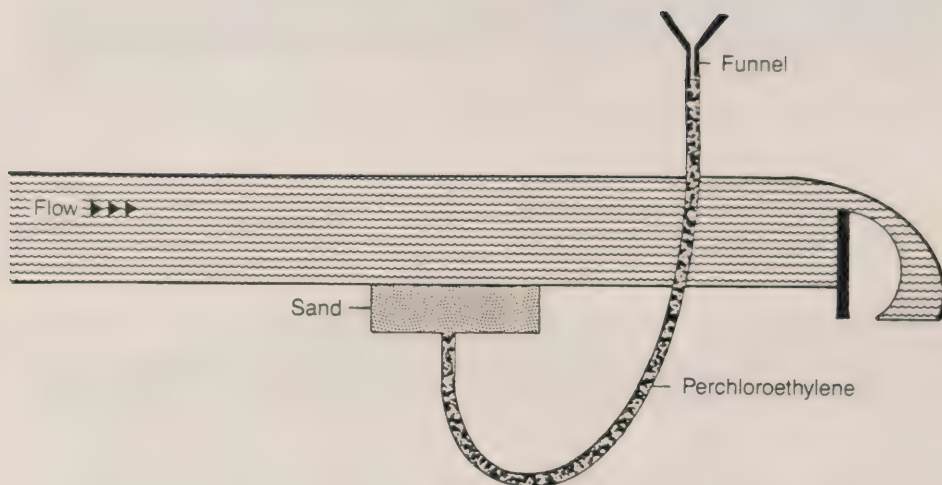


Figure 3.8 Experimental setup for feeding perchloroethylene to sand layer.

from outfalls or that leach into the river will spread, some calculations were made for the stretch of the St. Clair downstream from the CN tunnel, assuming the existence of point sources at several locations. These calculations were based on the stream tube model, as described in the mixing model RIVMIX. The flow parameters used were as follows:

Discharge	=	6510 m ³ /s
Depth	=	10.2 m
Velocity	=	1.04 m/s
Slope	=	0.000 025
Dispersion Coefficient	=	0.255 m ² /s

The approximate boundaries of three different plumes are shown in Figure 3.9. In general, it can be seen that the spreading rates of the plumes in the St. Clair are fairly slow.

Material that is released from the bank just downstream from the CN tunnel will occupy a plume of only about 150 m wide at a point some 2.5 km downstream. Material introduced at the centre of the river will not reach the bank for a very long distance downstream.

An MOE dispersion study in the St. Clair River (Hamdy and Kinkead, 1979) revealed that a dilution ratio of 20:1 was attained at a longitudinal distance of about 700 m and a lateral distance of 5 m from the source. A 100:1 dilution ratio was achieved at a longitudinal distance of 1.5 km and a lateral distance of 15 m. It is, therefore, evident that shore-based discharges result in a plumes confined to the Ontario shoreline with no transboundary pollution. In the river delta, mainly in the South Channel, transboundary pollution from the Ontario side

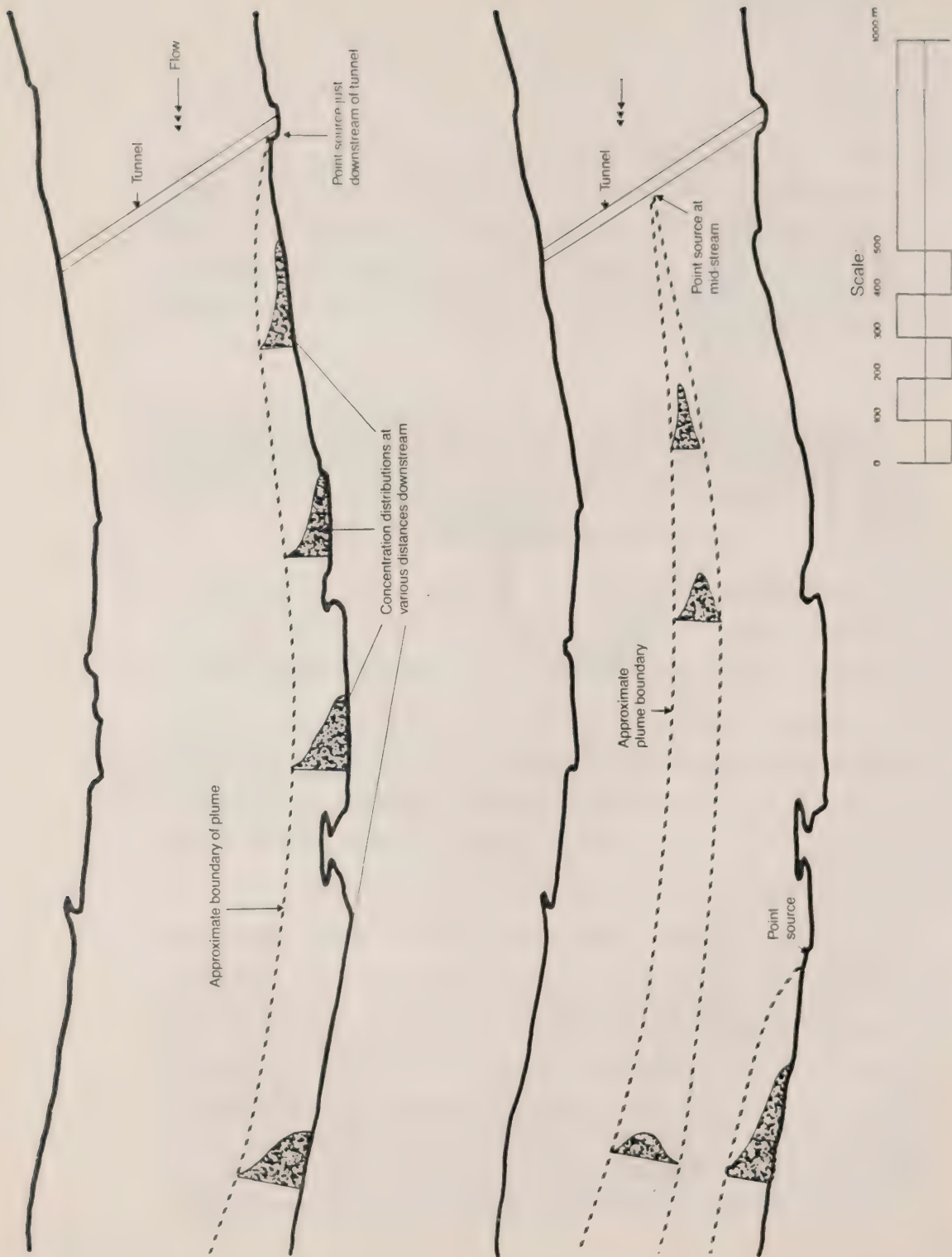


Figure 3.9 Plume boundaries and relative concentrations from several assumed point sources.

of the channel to the Michigan side does take place due to the meandering nature of the South Channel.

Sediment Transport Capacity and Sand Wave Characteristics

Estimates for sediment transport capacity were made for the area closer to the shore rather than for the river as a whole because of the smaller flow depth and probably smaller sediment size in the 100-m wide section adjacent to the shore.

The flow rate varies from $6510 \text{ m}^3/\text{s}$ to $5320 \text{ m}^3/\text{s}$. The flow depths were assumed to be 7.0 m to 6.0 m, respectively, for these two discharges. The median sand size was assumed to vary from 1.0 mm to 0.5 mm.

The sediment transport rate, calculated from the Ackers-White transport equation, varied from 1.5 to 2.7 tonnes per day per metre of river width. The length of the sand waves was calculated to be of the order of 40 m and the amplitude of the sand waves would vary between 0.75 m and 2.2 m.

It should be noted that these calculations were made based on equilibrium conditions of sediment supply and transport, i.e., there is enough sediment supply from Lake Huron to satisfy the sediment-carrying capacity of the river. If the supply is less than the carrying capacity, then it is likely that sand waves of smaller amplitude will be formed.

Based on the sediment transport rates mentioned above and the sand wave geometry, estimates of the velocities at which the sand waves progress downstream can be made. These calculations

show that the sand waves move at very low speeds, advancing only 4 to 5 m a day. Therefore it would take a sand wave about ten days to move past a given point.

Tests of Dissolution Rate

These tests were conducted in the flume by filling a tray with perchloroethylene and then running a flow of water over it for a period of time. The tray covered the full width of the flume and was 21 cm long and the top of the tray was flush with a bed of gravel which covered the flume. The level of the solvent in the tray was monitored using a point gauge and samples of the water discharging at the end of the flume were taken for analysis of perchloroethylene concentrations.

The tests were conducted using two different mean flow velocities at each of three water temperatures. Care was taken so that the maximum velocity used was below that at which perchloroethylene would be removed from the tray by the action of waves at the interface.

The test data show that, within the range of velocities and temperatures tested (0.1 to 0.2 m/s; 10°C to 20°C), the effect of these two parameters is only nominal. The average rate at which the perchloroethylene dissolved was about 40 g/h/m² of surface area. Thus it appears that the amount of perchloroethylene which would have been dissolved from the puddles found in the St. Clair would not be very large.

WATER SURVEY

Introduction

This section includes data from both federal and provincial agencies. Moreover, it provides results on water samples taken in both 1984 and 1985 at a variety of stations, from the upper St. Clair River to its mouth and into Lake St. Clair. It must be recognized that not only the sampling dates but also the sampling locations and depths vary considerably between the data sets. Furthermore, the analytical methodologies and, therefore, the number, types and detection limits for the contaminants differ substantially between the laboratories. Consequently, any interpretation of the results must take into consideration all of these variables.

Water Survey (DOE)

The water samples described in this section were collected in three phases:

- (1) During the spring of 1985, large-volume (200 L) water samples were collected from nearshore areas along the St. Clair River. The particulates from the centrifuged samples were analyzed separately.
- (2) During the summer of 1985, large-volume (40 L) water samples were collected on several occasions (August 7, August 27, September 24, October 16) from near Point Edward at the head of the river, near Port Lambton and near Windsor/Detroit at the head of the Detroit River.

The samples were collected at mid water column depth on transects across the river, with the samples from each transect being combined into one composite or mean sample for each transect. Whole water (suspended plus dissolved) samples and centrifuged suspended particulate samples were analyzed from each location.

- (3) During the latter part of November 1985, 60 water samples were collected from 20 transect lines on an 8-km reach of the river south of Sarnia. Three samples were collected along each transect 10, 25 and 100 m from shore (denoted by A, B and C, respectively). Bottom water samples were collected by either a vertical or horizontal Van Dorn sampler and transferred immediately to 250-mL bottles which were filled to exclude all air. Geographic locations of the sampling sites for the fall investigation are shown in Figure 3.10.

Analysis

The large-volume water samples were extracted using liquid-liquid extraction with dichloromethane or hexane. The extracts were then fractionated and analyzed using the same procedure as for the sediments.

For the analysis of the bottom water samples, a Hewlett-Packard 5880 gas chromatograph with a 30 m OV-1 capillary column was used. The temperature regime was a 2-min hold at -20°C , followed by a programming rate of $4^{\circ}\text{C}/\text{min}$ to 70°C . The instrument was run in split/splitless mode (1:15) with the initial

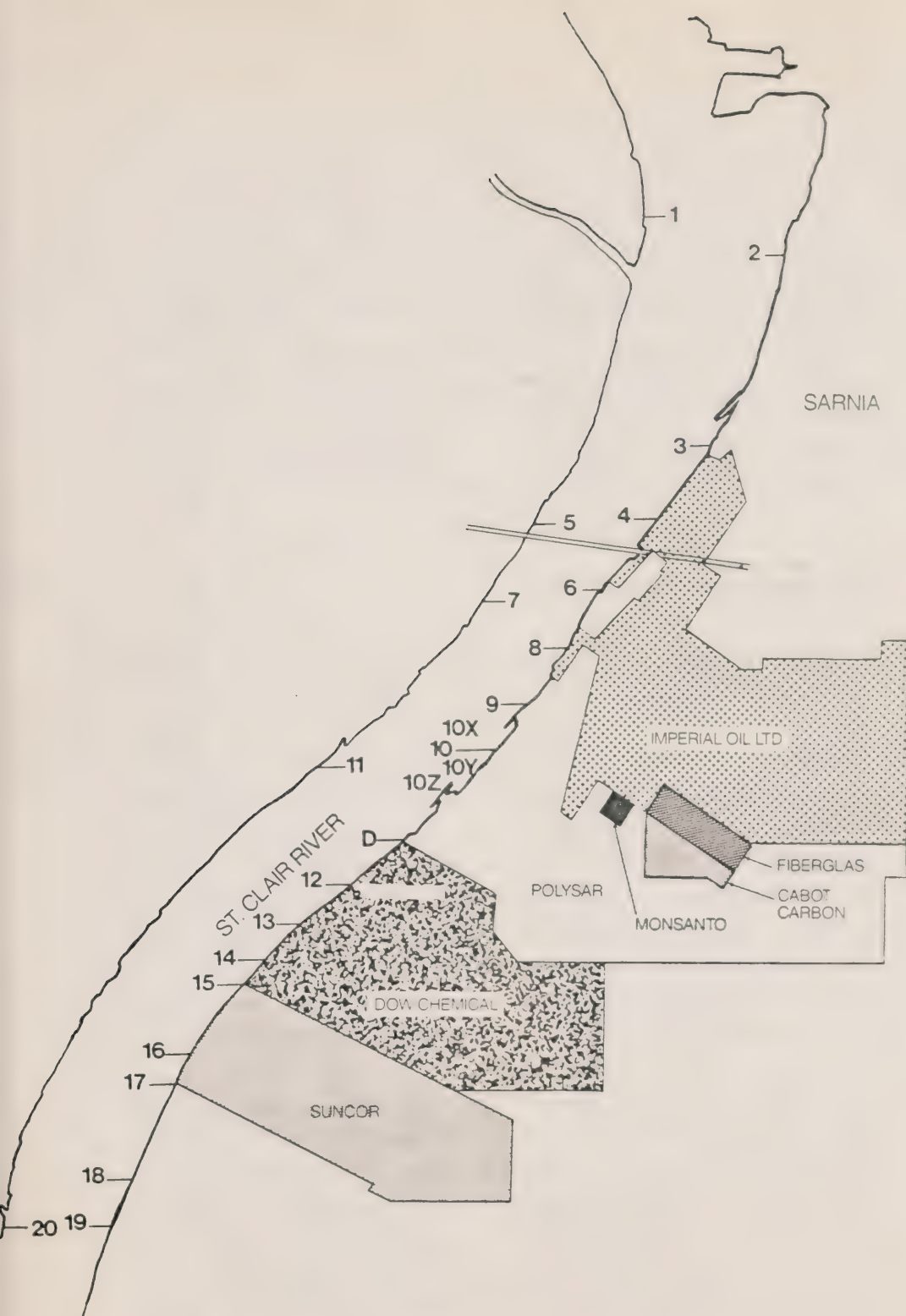


Figure 3.10 Sampling transects on St. Clair River at Sarnia, 1985.

0.2 min in splitless mode. Other instrument conditions were injector temperature, 80°C; electron capture detector temperature 280°C; carrier gas hydrogen, at 0.3 mL·min⁻¹. The presence of the following compounds was confirmed: perchloroethylene; carbon tetrachloride; chloroform; methylene chloride; 1,1,1-trichloroethane; trichloroethylene; 1,2-dichloroethylene; 1,1-dichloroethane; 1,2-dichloroethane; 1,1,2-trichloroethane; tribromomethane; and 1,1,2,2,-tetrachloroethane.

Near Shore Water Samples (1985)

The concentrations of HCE, HCB, QCB, HCB, and OCS in near shore water samples at the stations in Figure 3.11 are listed in Table 3.1. For illustration purposes, the changes in HCB concentrations along the river are shown in Figure 3.12. Dramatic increases in HCB concentrations (as well as the other four contaminants) occur after the Township ditch, with peak values reached near Dow. Elevated levels persisted for at least 25 km downstream. Since other sources of these chemicals are unlikely, these high downstream concentrations probably indicate that the effluent plume hugs the Canadian shoreline for a considerable distance. Low concentrations of these contaminants are observed at all stations on the western shore of the river.

Data for the four large-volume water samples collected from Point Edward, Port Lambton and at the head of the Detroit River during the summer of 1985 are shown in Figure 3.13 and Table 3.2. As was observed for the 1984 sediment data, the concentrations of contaminants were very low at the head of the St. Clair River. At Port Lambton the concentrations were one to two orders of magnitude higher for both the whole water samples

Table 3.1 Contaminant Concentrations in Near Shore Whole Water Samples from the St. Clair River, 1985
(ng/L or ppt)

Compound	WC-1	WC-2	WC-3	WC-4	WC-5	WC-6	WC-7	WC-8	WC-9	WC-10	WC-11
Hexachloroethane (HCE)	1.2	2.4	3.1	5.0	2.0	5.3	530	1700	110	90	41
Hexachlorobutadiene (HCBd)	0.4	0.8	0.7	0.9	4.6	7.8	130	160	76	12	73
Pentachlorobenzene (QCB)	ND	0.3	0.03	0.06	0.11	0.14	0.8	4.2	0.2	0.5	0.7
Hexachlorobenzene (HCB)	1.0	0.9	1.0	1.4	2.9	0.2	131	89	46	15	50
Octachlorostyrene (OCS)	0.09	0.2	0.09	0.03	0.03	0.03	11	7.6	3.6	1.1	2.6

Compound	WC-12	WC-13	WC-14	WC-15	WC-16	WU-1	WU-2	WU-3	WU-4	WU-5
Hexachloroethane (HCE)	80	17	38	27	14	1.2	2.8	4.8	20	ND
Hexachlorobutadiene (HCBd)	4.7	3.2	7.6	5.2	3.0	0.2	0.2	0.3	1.3	0.3
Pentachlorobenzene (QCB)	1.3	0.5	0.2	0.3	ND	ND	0.03	0.04	0.06	ND
Hexachlorobenzene (HCB)	11	13	2.9	3.7	2.8	0.1	0.3	0.2	0.6	0.7
Octachlorostyrene (OCS)	0.8	1.0	0.5	0.7	0.3	ND	ND	ND	0.02	ND

Table 3.2 The Concentrations of Hexachloroethane (HCE), Hexachlorobutadiene (HCBD), Hexachlorobenzene (HCB), and Octachlorostyrene (OCS) in Water and Suspended Sediments Collected on August 7, August 27, September 24, and October 16, 1985 from the St. Clair and Upper Detroit Rivers

Chemical	WHOLE WATER CONCENTRATIONS (ng/L)					
	Point Edward		Port Lambton		Windsor/Detroit	
	Head of St. Clair River		40 km Downstream of Sarnia		Head of Detroit River	
	Range	Mean	Range	Mean	Range	Mean
HCE	(0.005-0.6)	0.16	(0.5-6.9)	3.6	(0.02-0.2)	0.12
HCBD	(0.009-0.3)	0.09	(0.7-6.0)	2.3	(0.09-0.2)	0.15
HCB	(0.01-0.06)	0.03	(0.3-1.6)	0.8	(0.2-0.3)	0.22
OCS	(0.005-0.01)	0.008	(0.05-0.24)	0.12	(0.03-0.05)	0.04
	SUSPENDED SEDIMENT CONCENTRATIONS (ng/g)					
HCE	(ND*-0.6)	0.5**	(0.1-1.2)	0.5	(ND-0.2)	0.2**
HCBD	(ND-1.1)	1.0**	(8-44)	20	(1.7-3.5)	2.4
HCB	(ND-2.9)	2.0**	(60-240)	130	(15-29)	21
OCS	(ND-0.8)	0.7**	(10-39)	23	(3.8-7.0)	4.8

* Not Detected

** Mean of Detected Values

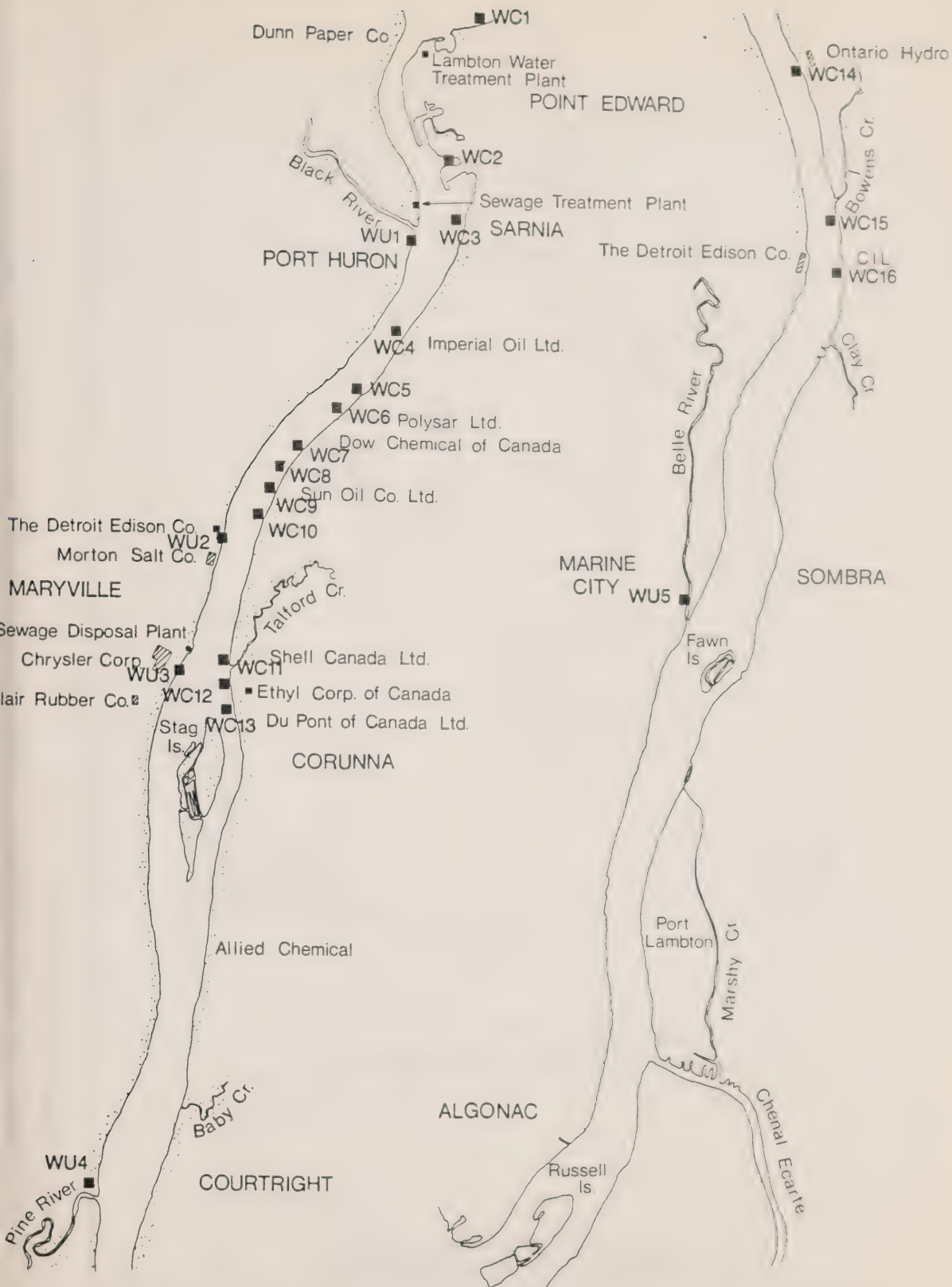


Figure 3.11 Sampling stations, St. Clair River, 1985.

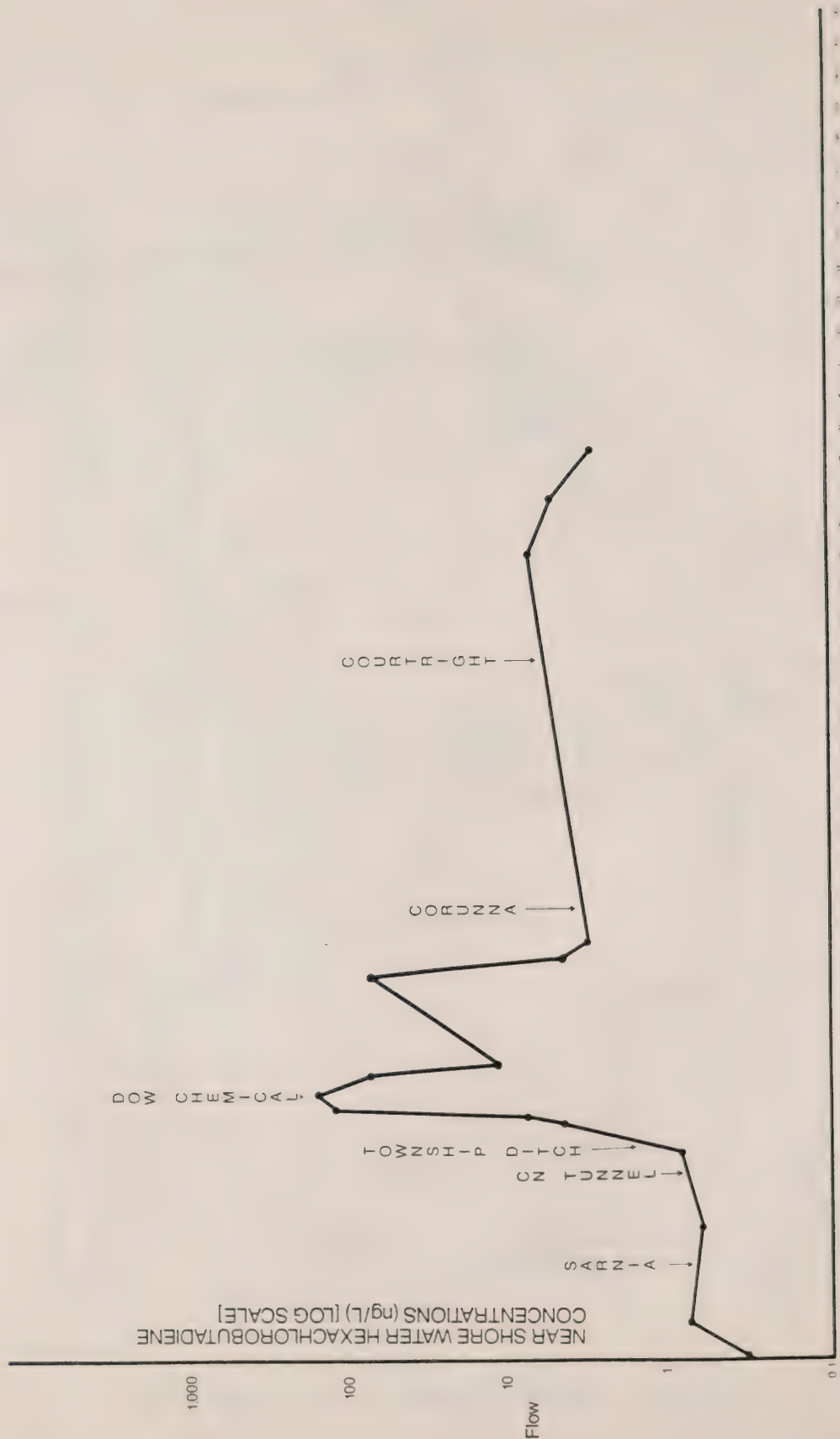


Figure 3.12 HCB concentrations in near shore water of St. Clair River (ug/L) [log scale].

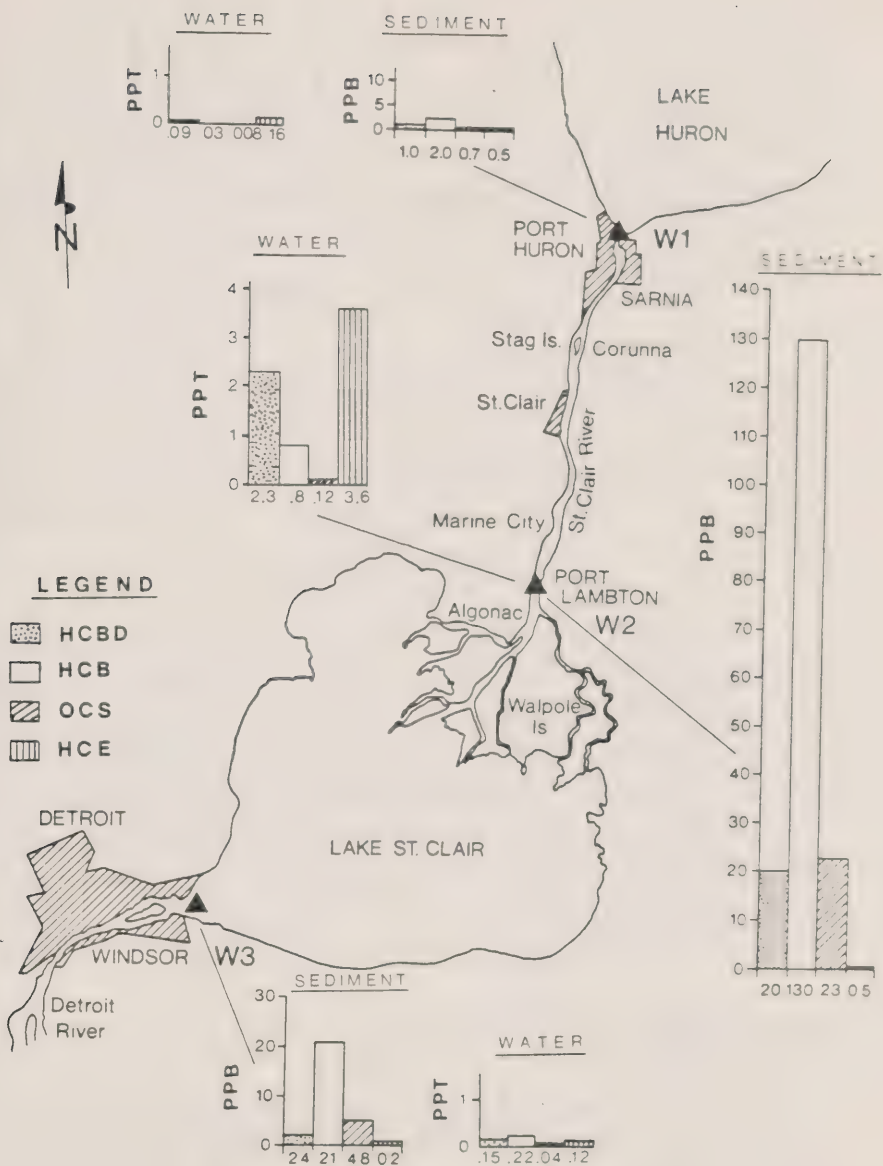


Figure 3.13 HCB, HCE, OCS and HCB concentrations in suspended sediment (ppb) and water (ppt), 1985.

and the suspended sediment samples except for the hexachloroethane in suspended sediment which showed no increase over Point Edward. Hexachloroethane is a volatile compound with a very weak tendency to adsorb onto sediment material. The contaminant concentrations in whole water samples observed at Port Lambton were very low (≤ 3.6 ng/L or ppt).

Elevated concentrations of contaminants were observed at the head of the Detroit River compared with the head of the St. Clair River for HCB, HCB and OCS, but concentrations were much lower than at Port Lambton. These data show that significant chemical losses occur in Lake St. Clair, but that there is some chemical residual carry over to the Detroit River.

The results of the November 1985 bottom water survey are summarized in Table 3.3 for the four major volatile halocarbon contaminants at the 60 sampling stations. For comparison, the data for a water sample from the Township ditch (TSD) are also given in Table 3.3. The Township ditch data show elevated values of volatile contaminants especially chloroform which is both an industrial solvent and a by-product of the chlorination of raw and waste water.

RECOMMENDATION

Sources of volatile hydrocarbons in the Township ditch should be investigated and action be initiated to reduce these compounds drastically.

Table 3.3. Concentration of the Four Major Volatile Halocarbon Contaminants in the Upper St. Clair River (ng.L⁻¹)

Station No.	2A	2B	2C	3A	3B	3C	4A	4B	4C	6A	6B	6C	8A	8B	8C
ng.L ⁻¹ PERC	2	2	3	3	12	2	6	5	489	21	2	6	2	2	10
ng.L ⁻¹ CTC	16	2	3	5	11	3	15	2411	48	7	2	7	5	4	5
ng.L ⁻¹ 1,1,1TCA	4174	5	12	7	5	6	21	18	25	12	12	9	9	8	10
ng.L ⁻¹ CHCl ₃	35	5	8	10	9	5	10	12	8	10	20	8	6	6	12

Station No.	9A	9B	9C	10A	10B	10C	12A	12B	12C	13A	13B	13C	14A	14B	14C
ng.L ⁻¹ PERC	4	2423	71	246	2	12	552	409	8	646	259	4	440	156	9
ng.L ⁻¹ CTC	3	4	7	177	6	4	747	289	4	1210	389	5	544	117	8
ng.L ⁻¹ 1,1,1TCA	22	19	19	21	10	8	330	101	9	456	148	7	230	70	8
ng.L ⁻¹ CHCl ₃	11	7	11	13	15	134	46	54	27	65	28	17	34	183	7

Station No.	15A	15B	15C	16A	16B	16C	17A	17B	17C	18A	18B	18C	19A	19B	19C
ng.L ⁻¹ PERC	593	474	95	438	181	33	740	471	399	464	495	102	253	556	170
ng.L ⁻¹ CTC	511	462	36	472	166	29	427	274	192	249	269	105	286	338	164
ng.L ⁻¹ 1,1,1TCA	224	198	15	220	82	13	196	127	89	111	118	44	125	143	60
ng.L ⁻¹ CHCl ₃	72	36	28	52	17	24	37	32	58	273	33	24	30	65	32

Station No.	1A	1B	1C	5A	5B	5C	7A	7B	7C	11A	11B	11C	20A	20B	20C	TSD
ng.L ⁻¹ TECE	8	4	5	5	5	4	663	8	7	2	6	5	4	2	2	567
ng.L ⁻¹ CTC	4	3	51	5	36	6	4	3	4	2	2	2	3	3	2	95
ng.L ⁻¹ 1,1,1TCA	23	10	7	24	26	20	43	41	16	11	12	12	8	8	7	103
ng.L ⁻¹ CHCl ₃	30	8	10	26	17	6	14	13	10	9	9	9	12	8	26	4482

Discussion

Figure 3.14 shows a bar graph of the perchloroethylene concentrations in a logarithmic plot by stations. As evident, low concentrations of 1 to 10 $\text{ng}\cdot\text{L}^{-1}$ are prevalent in the samples from both near shore and offshore stations on the western shore of the river (stations 1, 5, 7, 11 and 20). Except for two samples, the same is observed for the upstream locations on the eastern shore (stations 2, 3, 4, 6 and 8). Downstream from station 8, near shore stations (A and B) show strongly elevated concentrations throughout. In fact, the highest value observed, 2411 $\text{ng}\cdot\text{L}^{-1}$, was found at station 9B. This level is well within the U.S. EPA ambient water quality criterion of 9000 $\text{ng}\cdot\text{L}^{-1}$ for the protection of aquatic life (CCREM Task Force, 1985). It is further apparent that there are steady to slightly declining perchloroethylene levels in the nearshore samples (A and B) downstream from station 12. At the same time, the perchloroethylene concentrations in the offshore samples (C) increase between stations 12 and 19. This observation is consistent with plume models derived from experimental observations (vide infra) which show the slow spreading of a contaminant plume from multiple inputs along the river shore.

RECOMMENDATION

Possible sources of the carbon tetrachloride and perchloroethylene upstream from the CN tunnel should be investigated.

If the perchloroethylene levels of approximately 500 $\text{ng}\cdot\text{L}^{-1}$ observed at stations 17 and 19 can be considered to represent average values, and given a mean velocity of approximately

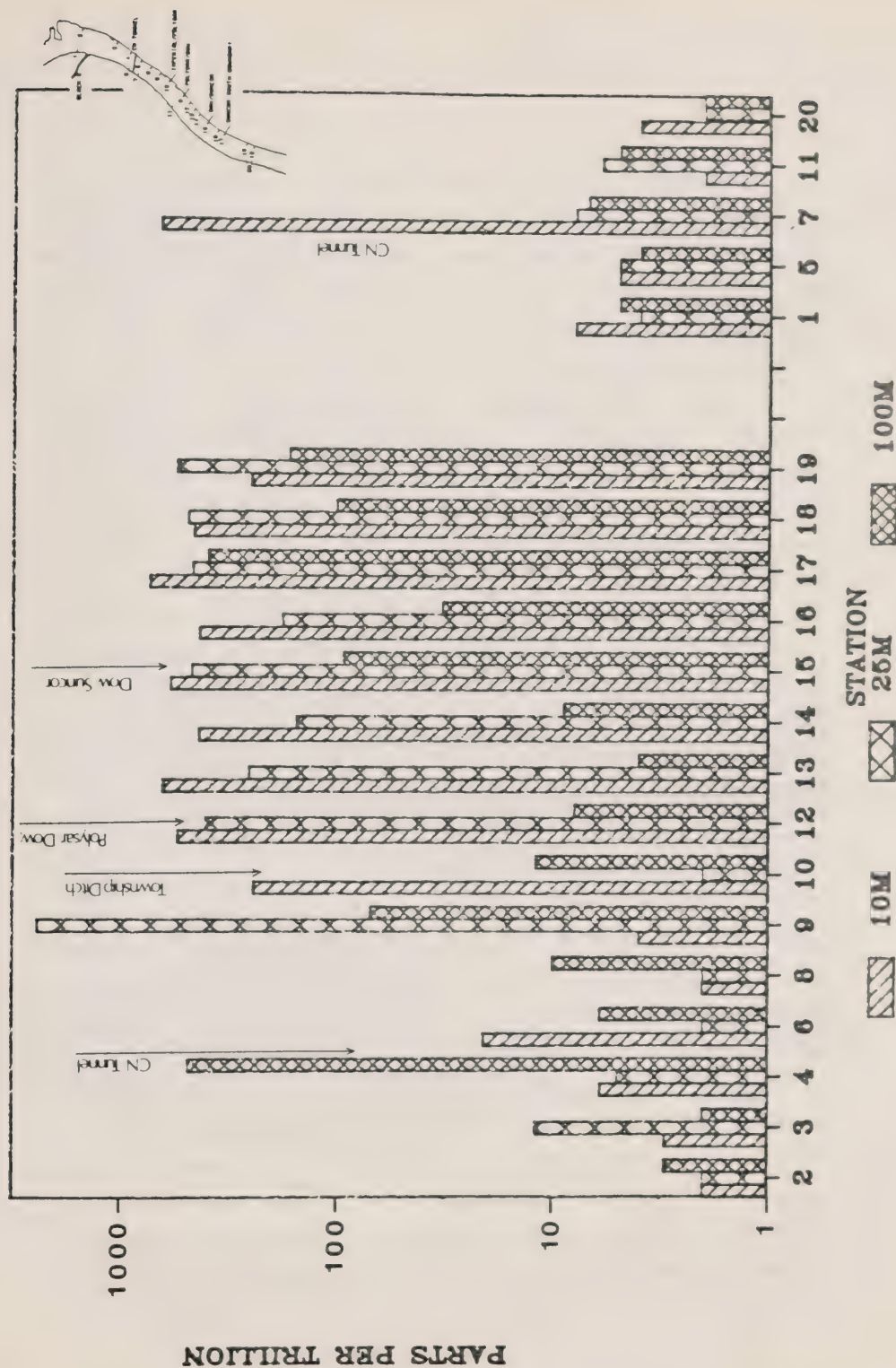


Figure 3.14 Logarithmic scale bar graph of perchloroethylene concentrations (ng.L⁻¹) in the upper St. Clair River, 1985.

$1 \text{ m} \cdot \text{s}^{-1}$ (Derecki, 1984), and mean depths of 4, 7 and 10 m at the substations A, B, and C, respectively, the total mass of perchloroethylene moving downstream can be calculated to be approximately $32 \text{ kg} \cdot \text{day}^{-1}$. This loading figure is consistent with those calculated from various industrial sewer outfalls. For example, the four sewers at the 1st Street area (near station 12) have been shown to contribute approximately $30 \text{ kg} \cdot \text{day}^{-1}$ (vide infra). Although their combined flow is only a fraction of that of all outfalls along the St. Clair River, perchloroethylene concentrations as high as $1.1 \times 10^6 \text{ ng} \cdot \text{L}^{-1}$ have been observed in these effluents. The loading calculated from the present transect data ($32 \text{ kg} \cdot \text{day}^{-1}$) is also consistent with that calculated from Lake St. Clair data, which is $48 \text{ kg} \cdot \text{day}^{-1}$, based on a mean of $209 \pm 125 \text{ ng} \cdot \text{L}^{-1}$ perchloroethylene at 13 stations in the St. Clair River delta and northern parts of Lake St. Clair. The perchloroethylene distribution in Lake St. Clair, based on surface water samples taken in the summer of 1984, is shown in Figure 3.15 (Kaiser and Comba, 1985).

Figure 3.16 shows a similar bar graph of carbon tetrachloride concentrations. As for perchloroethylene, the carbon tetrachloride levels are in the range of 1 to $10 \text{ ng} \cdot \text{L}^{-1}$ for most stations along the western shore and also the upstream stations on the eastern shore (stations 2, 3, 6, 8 and 9). However, a carbon tetrachloride concentration of over $2000 \text{ ng} \cdot \text{L}^{-1}$ was found at station 4B, just upstream from the railway tunnel. Strongly elevated levels were also observed at all sites downstream from station 10A. Again as for perchloroethylene, the input of carbon tetrachloride appears primarily to be in the near shore zone (stations A and B), as evident from the pronounced concentration gradients between the near shore and offshore (station C) zones sampling sites 10 to 14. This gradient diminishes in a

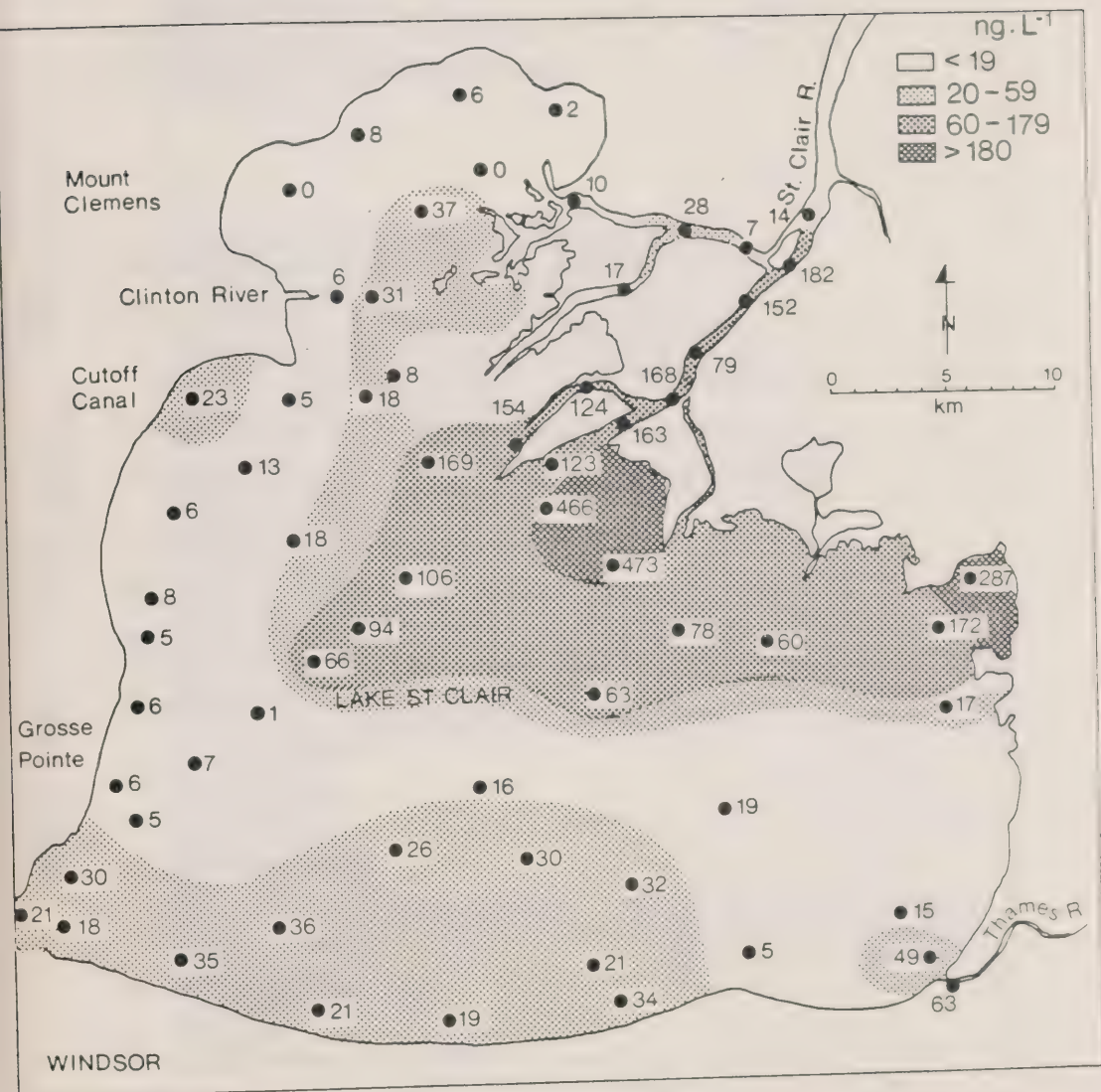


Figure 3.15 Distribution of perchloroethylene in Lake St. Clair and lower St. Clair River surface water samples in summer of 1984.

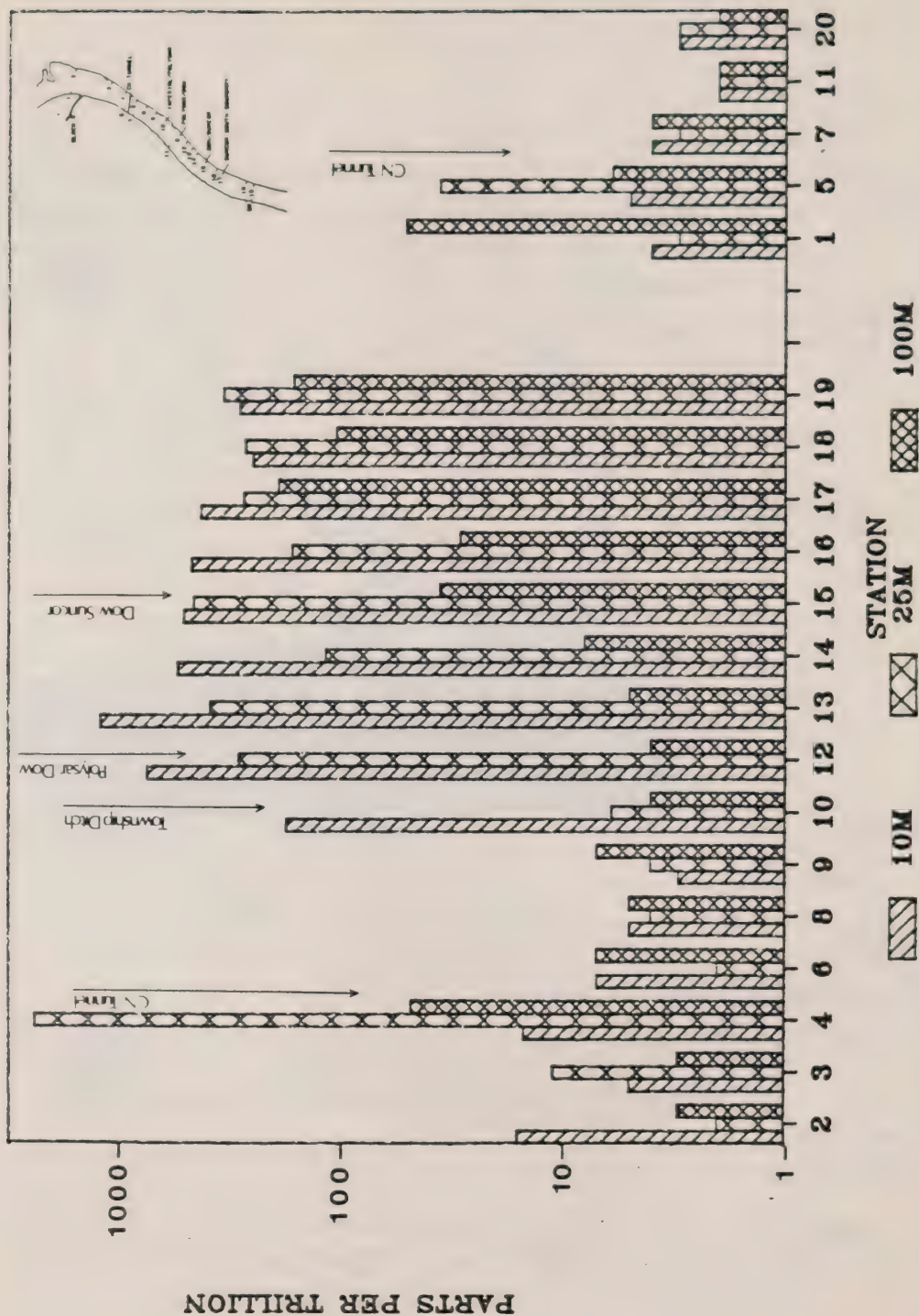


Figure 3.16 Logarithmic scale bar graph of carbon tetrachloride concentrations (ppb)

downstream direction and the concentrations at the offshore stations 17C, 18C and 19C are close to those of the respective near shore values.

According to the U.S. EPA Ambient Water Quality Criteria for carbon tetrachloride of 7000 ng L^{-1} (CCREM Task Force, 1985), levels in the ambient water are well within the range for the preservation of aquatic life.

Taking the observed mean carbon tetrachloride concentration at station 19 as $326 \pm 203 \text{ ng} \cdot \text{L}^{-1}$, a continuous loading of approximately $21 \text{ kg} \cdot \text{day}^{-1}$ is calculated. This compares with the approximately $75 \text{ kg} \cdot \text{day}^{-1}$ calculated from concentrations in the St. Clair River delta and Lake St. Clair, as shown in Figure 3.17 (Kaiser and Comba, 1985).

Figure 3.18 shows a bar graph of 1,1,1-trichloroethane (111-TCA) in the same bottom water samples. Except for one very high value at the nearshore station 2A, its concentrations generally range between 10 and $500 \text{ ng} \cdot \text{L}^{-1}$. However, as for perchloroethylene and carbon tetrachloride, a sharp increase of 111-TCA levels is observed for the near shore station 12A and downstream from there. Again, slow horizontal mixing of the plume is evident between stations 12 and 19, resulting in increased concentrations at the offshore stations when going downstream. Assuming a mean of approximately $100 \text{ ng} \cdot \text{L}^{-1}$, a loading of $3 \text{ kg} \cdot \text{day}^{-1}$ 1,1,1-trichloroethane is estimated.

Figure 3.19 shows a logarithmic scale bar graph for chloroform concentrations at the 60 sampling sites. In general, levels of 10 to $20 \text{ ng} \cdot \text{L}^{-1}$ are observed on both sides of the river. As for the other volatile contaminants, increased levels are found

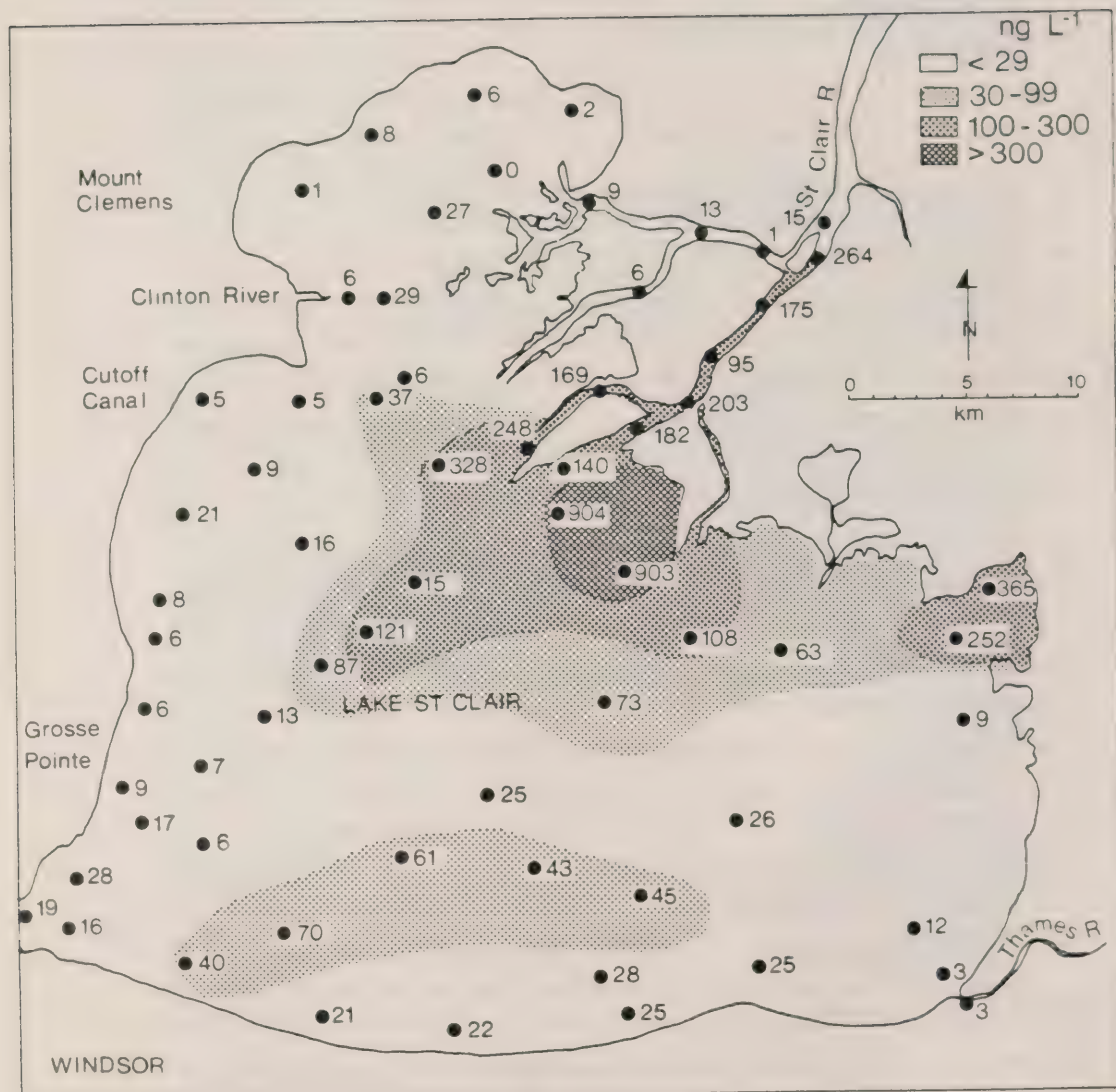


Figure 3.17 Distribution of carbon tetrachloride in Lake St. Clair and lower St. Clair River surface water samples in summer of 1984.

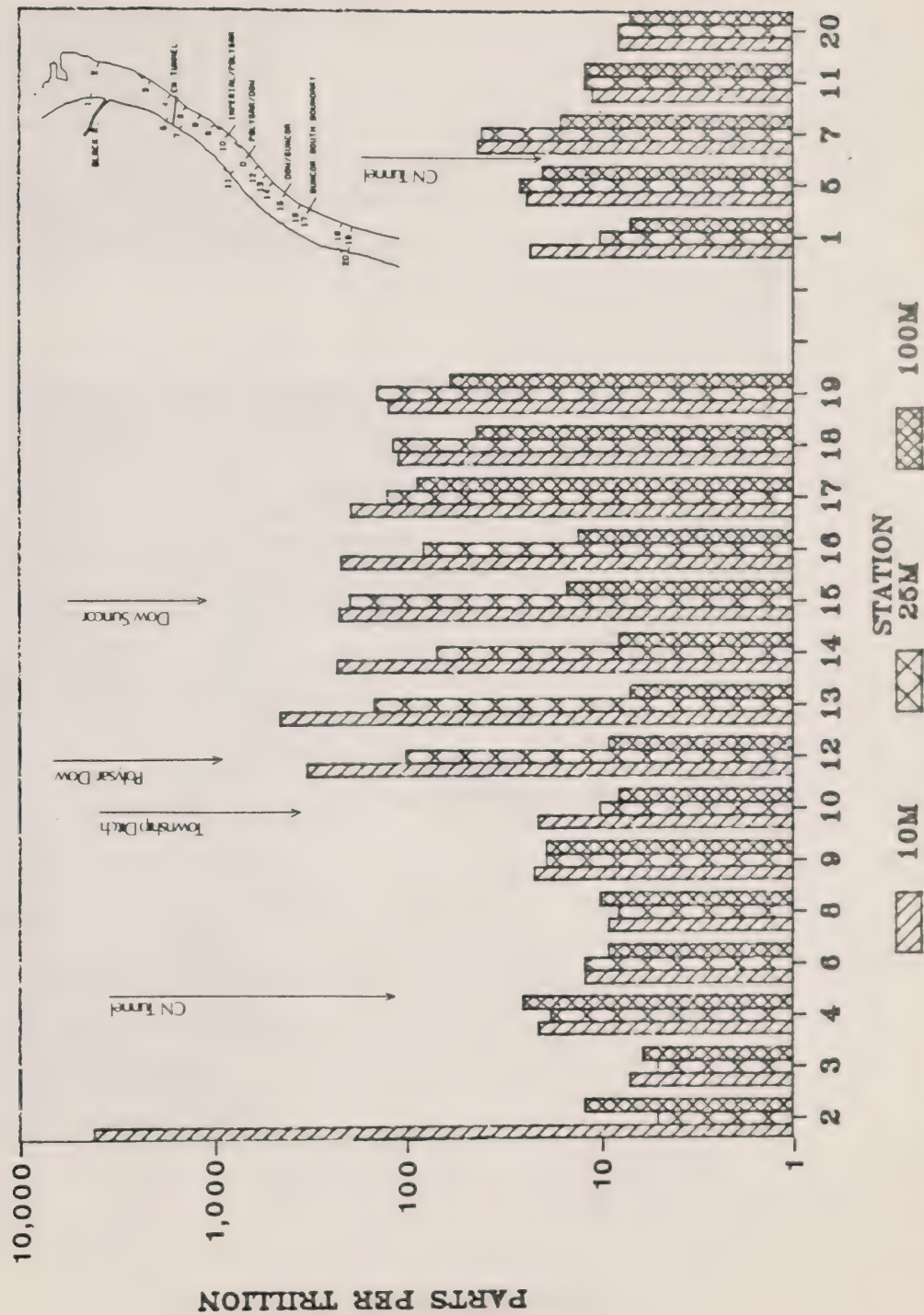
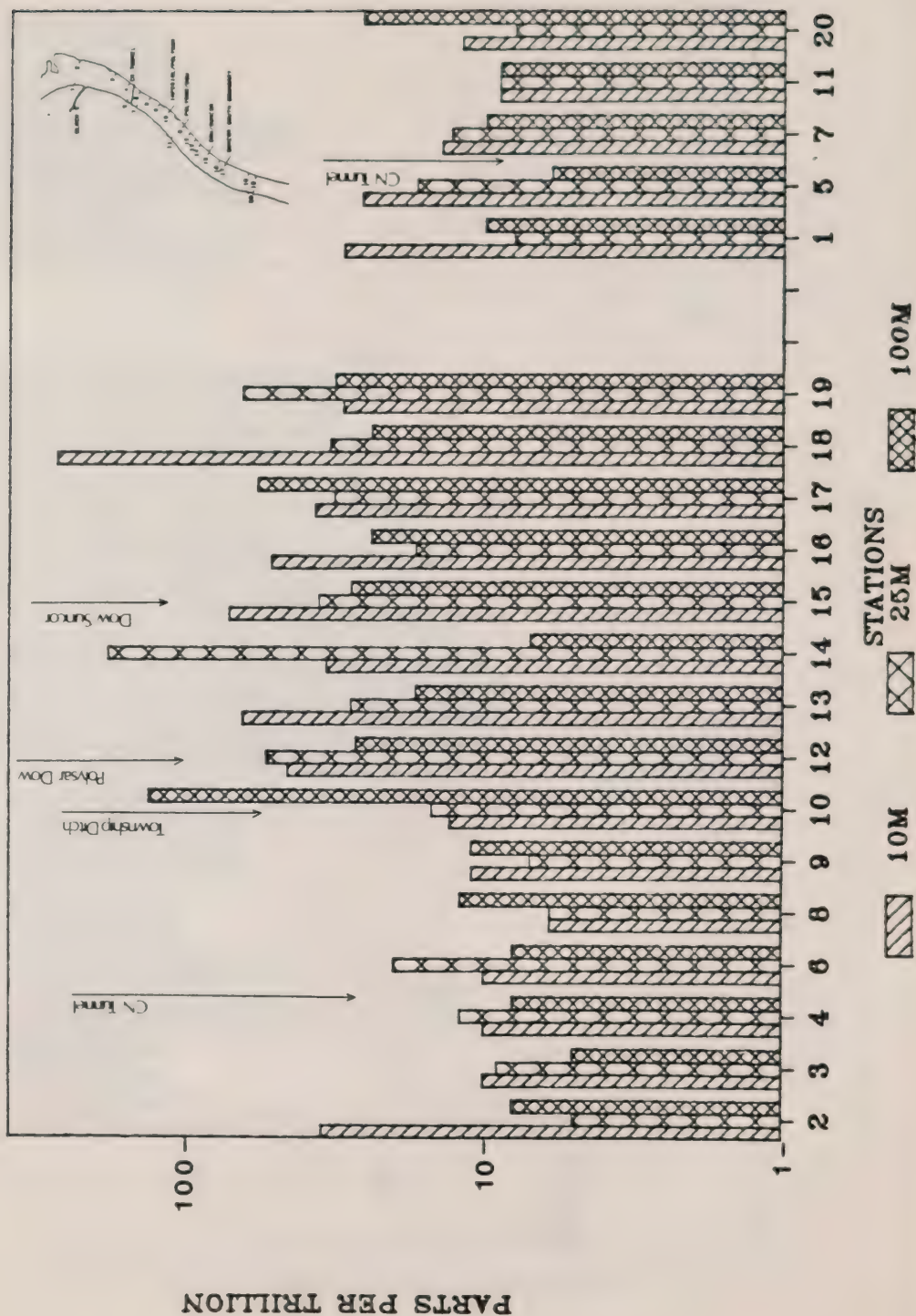


Figure 3.18 Logarithmic scale bar graph of 1,1,1-trichloroethane concentrations (ng.L⁻¹) in the upper St. Clair River, 1985.



downstream from station 10, with the highest level of $273 \text{ ng}\cdot\text{L}^{-1}$ found at station 18A which is well below the U.S. EPA ambient water quality criterion of $15\,700 \text{ ng}\cdot\text{L}^{-1}$ for the protection of aquatic life. In contrast to perchloroethylene, carbon tetrachloride, and 1,1,1-trichloroethane, chloroform is primarily a by-product of raw and waste water chlorination and its industrial use as solvent or process material is smaller. The observed concentrations are to be expected from the large volume of cooling water discharged along the St. Clair River. In addition, intermittent chloroform discharges between stations 10 and 19 are apparent from the strong fluctuations of the chloroform levels in that reach of the river. Similarly, fluctuating levels of chloroform were observed in water samples from Lake St. Clair in the summer of 1984, indicating intermittent discharges of higher concentrations on lower level background concentrations in the upper St. Clair River.

Water Survey (MOE)

The Ontario Ministry of the Environment (MOE) initiated monitoring activities in the St. Clair River in the late 1960's. At this time emphasis was focused on total phenols, a parameter associated with the refineries and petrochemical industry. Violations of the 1978 Great Lakes Water Quality Agreement Objectives for phenol ($1 \mu\text{g/L}$) were prevalent during the period 1969 to 1978 (Fig. 3.20). The introduction of biological oxidation treatment facilities at most of the industrial plants (1979-1982) resulted in significant reduction of phenol levels in the St. Clair River. Currently, phenol levels are well within the Agreement Objectives.

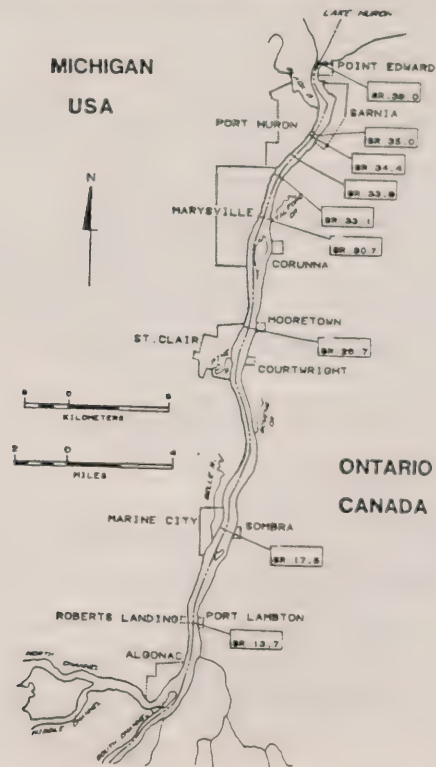
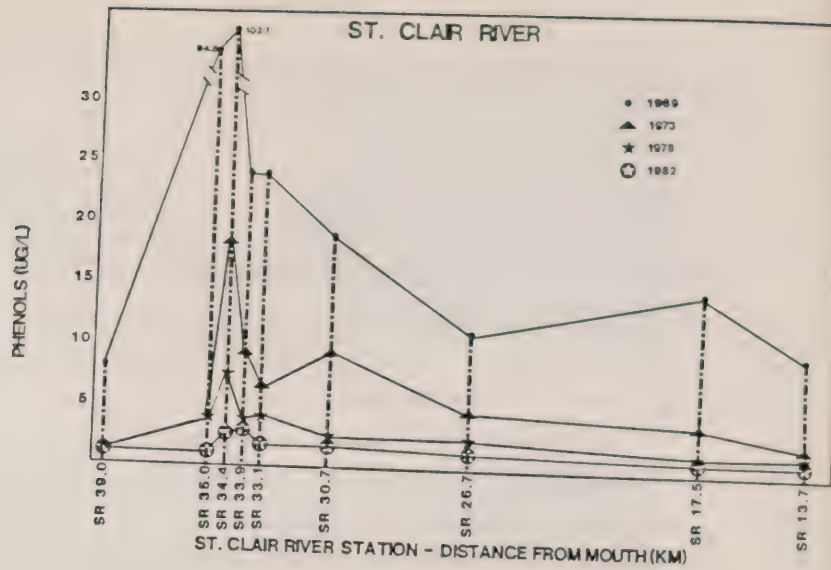


Figure 3.20 Phenol trends in the St. Clair River.

Extensive survey work by MOE to determine the environmental impact of organic contaminants has been ongoing since 1977 (Bonner and Meresz, 1981). A preliminary investigation in 1982, as part of a biological monitoring of organochlorine contaminants in the St. Clair River (Kaus and Hamdy, 1985), revealed that organic compounds such as hexachlorobenzene, octachlorostyrene, pentachlorobenzene and hexachlorobutadiene were restricted to the Ontario shoreline of the river.

During a follow-up survey (May-October, 1984), 17 stations were monitored along the Ontario shoreline of the St. Clair River, and 4 stations along the Michigan side of the river for chlorinated organics (Fig. 3.21). This water monitoring program was part of a biomonitoring investigation using caged clams. Ten chlorinated organic contaminants were detected along the Ontario shoreline of the river. Concentrations along the Michigan shoreline were all below the detection limit.

Chlorinated organics such as hexachlorobenzene, octachlorostyrene, hexachlorobutadiene, hexachloroethane, pentachlorobenzene, 2,4,5-trichlorotoluene, trichlorobenzene and tetrachlorobenzene were found at elevated levels in a 1.8-km section of the riverfront from the Township ditch to the Dow/Suncor property line (Figure 3.22a, 3.22b). Additional, although generally smaller, inputs of these materials also occur in the 1-km section from the mouth of the Talford Creek to the bottom end of Petrosar.

At 100 m downstream from the 1st Street sewer complex, the following average and maximum levels were observed (based on 7 samples) (Table 3.4). Total PCBs were not observed at a

Table 3.4. Chlorinated Organics, 1984 MOE Survey

Compound	Average (ng/L)	Maximum (ng/L)	Detection Limit (ng/L)
Hexachloroethane	200	825	1
Hexachlorobutadiene	400	1300	1
Hexachlorobenzene	400	2400	1
Octachlorostyrene	27	140	1
Pentachlorobenzene	5	150	1
1,2,4-Trichlorobenzene	500	1700	5
1,2,3,5-Tetrachlorobenzene	11	74	1
1,2,4,5-Tetrachlorobenzene	4	20	1

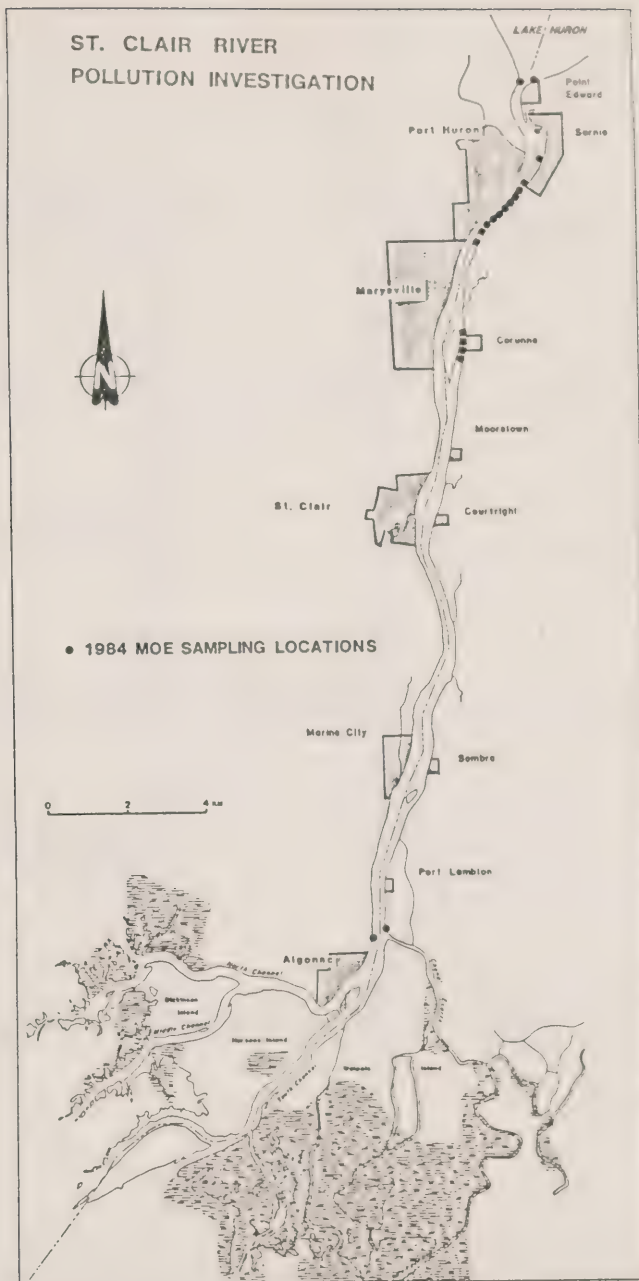


Figure 3.21 1984 MOE St. Clair River sampling locations.

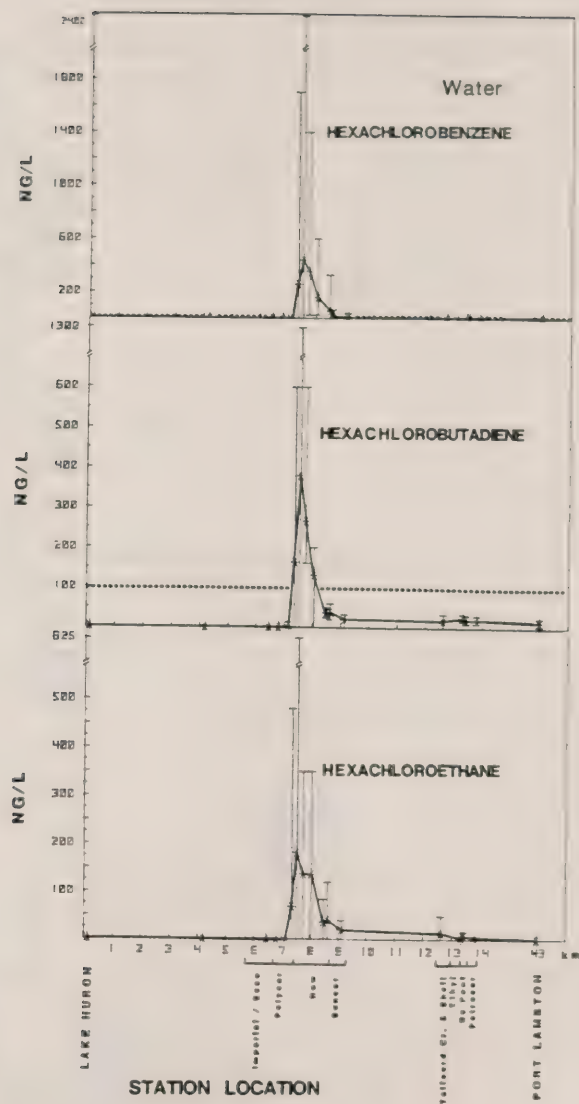


Figure 3.22a 1984 St. Clair River chlorinated organic compounds in water.

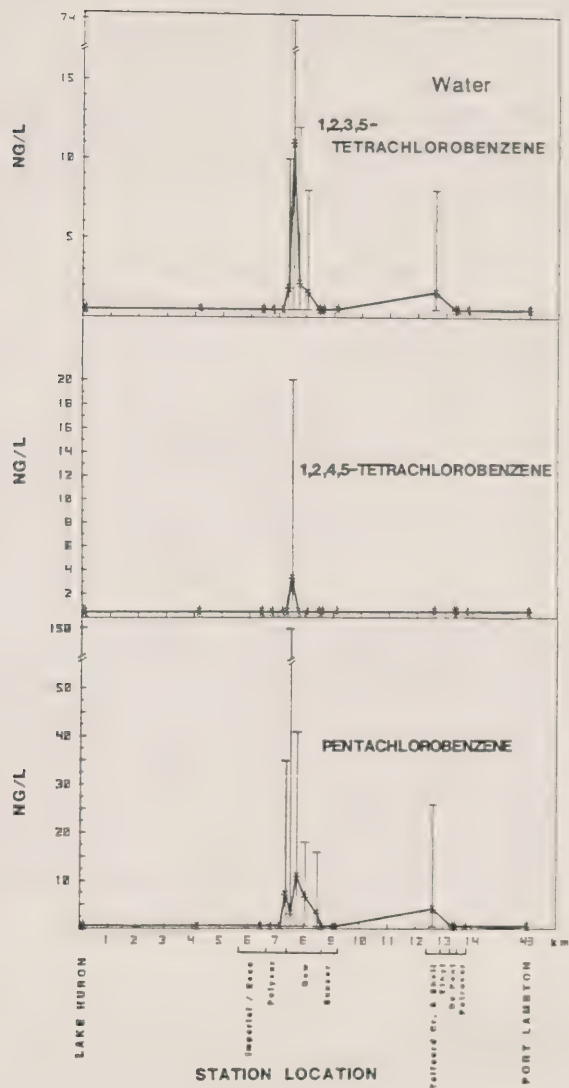


Figure 3.22b 1984 St. Clair River chlorinated organic compounds in water.

detection limit of 20 ng/L, although detected in caged clams at levels ranging from 20 ng/g to 180 ng/g.

The range of concentrations observed in the water column in the vicinity of Dow's 1st Street sewer complex suggests inputs which are highly variable in magnitude.

Using the maximum values observed, the magnitude of exceedances for existing or proposed objectives or criteria for the protection of aquatic life (McCarty et al., 1984) are:

- 370-fold for hexachlorobenzene
- 13-fold for hexachlorobutadiene
- 5-fold for pentachlorobenzene
- 3-fold for 1,2,4-trichlorobenzene

At a distance of 600 m downstream from Dow's 1st Street sewer complex, calculations based on one of the seven sampling events indicated that the level of hexachlorobenzene would exceed the proposed criterion for this compound by approximately 100 times. This indicates the importance of obtaining reductions of hexachlorobenzene at source, especially considering the toxicity and persistence of this compound and the fact that it is categorized as a potential carcinogen.

RECOMMENDATION

Immediate action should be initiated to reduce hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD) levels in the 1st Street sewer outfalls.

In response to the August 1985 perchloroethylene spill by Dow Chemical, a one-week intensive survey was undertaken by MOE beginning September 23. One component of this survey investigated volatile organic compounds (Table 3.5) measured in surface and bottom ambient waters from the southern end of Imperial Oil (just above the Township ditch) to the southern end of Suncor (Fig. 3.23).

Using a GC purge and trap technique, detection limits of $1 \mu\text{g/L}$ (1 ppb) were established. A detection limit in the ppt range, as employed by DOE during their November survey, was not warranted, since ambient concentrations remained high due to the spill. Results are presented in Table 3.6. Perchloroethylene and carbon tetrachloride distribution patterns are illustrated in Figures 3.24 and 3.25, respectively.

Volatile compounds were absent (detection limit $1 \mu\text{g/L}$) at the upstream location situated just above the Township ditch. A number of compounds including perchloroethylene, carbon tetrachloride, tri- and tetrachloroethane isomers and trichloroethylene were detected in bottom water, both adjacent to and 6 m upstream from the 1st Street sewers. This latter station may have received contaminants through the action of back eddies which commonly occur in near shore areas of the river.

Along a transect opposite Dow's 1st Street sewers, the surface levels of perchloroethylene decreased with distance offshore ($159 \mu\text{g/L}$ at 10 m offshore, $59 \mu\text{g/L}$ at 20 m offshore, and $1 \mu\text{g/L}$ at 40 m offshore), whereas the bottom levels increased and reached $83 \mu\text{g/L}$ at 40 m offshore. These levels persisted in the bottom waters at 30 m offshore at a point 20 m downstream from the 1st Street sewer complex. All are above the U.S. EPA water quality criterion of $9 \mu\text{g}\cdot\text{L}^{-1}$ for the protection of aquatic life.

Table 3.5 Compounds Tested in Surface and Bottom Waters, 1985
MOE Survey

1,1-Dichloroethylene	Chlorodibromoethane
Dichloromethane	Perchloroethylene
Trans-1,2-Dichloroethylene	Chlorobenzene
Dichloroethane	Trifluorochlorotoluene
Chloroform	Total Trihalomethane
1,1,1-Trichloroethane	Ethylbenzene
1,2-Dichloroethane	P-xylene
Carbon tetrachloride	M-xylene
Benzene	Bromoform
1,2-Dichloropropane	O-xylene
Trichloroethylene	1,1,2,2-tetrachloroethane
Dichlorobromomethane	1,4-Dichlorobenzene
Toluene	1,3-Dichlorobenzene
1,1,2-Trichloroethane	1,2-Dichlorobenzene

Table 3.6 Volatile Hydrocarbons ($\mu\text{g/L}$) in the St. Clair River

Upstream from Dow's 1st Street Sewer Complex		
	Surface	Bottom
Perchloroethylene	2	22
1,1,1-Trichloroethane	< 1	4
Carbon tetrachloride	< 1	5
Trichloroethylene	< 1	2
1,1,2-Trichloroethane	< 1	5
1,1,2,2-Tetrachloroethane	< 1	2
Plume adjacent to 1st Street Sewer Outfalls		
Dichloroethane	13	
Chloroform	87	
1,1,1-Trichloroethane	21	
Carbon tetrachloride	665	
Benzene	11	
Trichloroethylene	42	
1,1,2-Trichloroethane	21	
Perchloroethylene	1120	
Total Trihalomethane	87	
1,1,2,2-Tetrachloroethane	4	

- Upstream from Township ditch.

- No purgeable compounds were detected (detection limit 1 ppb).

Table 3.6 Continued

Transect Opposite 1st Street Sewer Complex						
	Distance from Shore					
	10 m		20 m		40 m	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1,1-Dichloroethylene	4	<1	<1	<1	<1	<1
Dichlorethane	5	<1	<1	<1	<1	<1
Chloroform	4	<1	<1	<1	<1	<1
1,1,1-Trichloroethane	<1	2	5	<1	<1	<1
Carbon tetrachloride	8	3	6	2	<1	4
Benzene	<1	<1	<1	<1	14	<1
Trichloroethylene	9	<1	3	<1	<1	<1
1,1,2-Trichloroethane	13	<1	5	<1	<1	<1
Perchloroethylene	159	33	59	14	<1	83
Trihalomethanes	4	<1	<1	<1	<1	<1
1,1,2,2-Tetrachloroethane	4	<1	2	<1	<1	<1

Transect 20 m Downstream from 1st Street Sewer Complex	
	Distance from Shore
	30 m
	Bottom
Chloroform	2
1,1,1-Trichloroethane	2
Carbon tetrachloride	70
Benzene	2
Perchloroethylene	68
Trihalomethanes	2

Table 3.6 Continued

300 m Downstream from Dow 1st Street Sewer Complex (Above 2nd Street Sewer)						
	Distance from Shore					
	10 m		20 m		40 m	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1,1,2-Trichloroethane	4	< 1	4	< 1	< 1	< 1
Perchloroethylene	75	26	35.5	11	< 1	18
1,1-Dichloroethylene	2	< 1	1.5	< 1	< 1	< 1
Dichlorethane	11	< 1	10.5	< 1	< 1	< 1
1,1,1-Trichloroethane	13.5	< 1	13.5	< 1	< 1	< 1
1,2-Dichloroethane	14.5	< 1	16	< 1	< 1	< 1
Carbon tetrachloride	5.5	< 1	9	7	2	8
Trichloroethylene	2.5	< 1	3	< 1	< 1	< 1
Benzene	< 1	14	< 1	23	< 1	10
Southern End of Suncor 1800 m Downstream from Dow 1st Street Sewer Complex						
	Distance from Shore					
	10 m		20 m		40 m	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
Carbon tetrachloride	5	6	5	5	5	4
Perchloroethylene	8	12	8	10	9	6

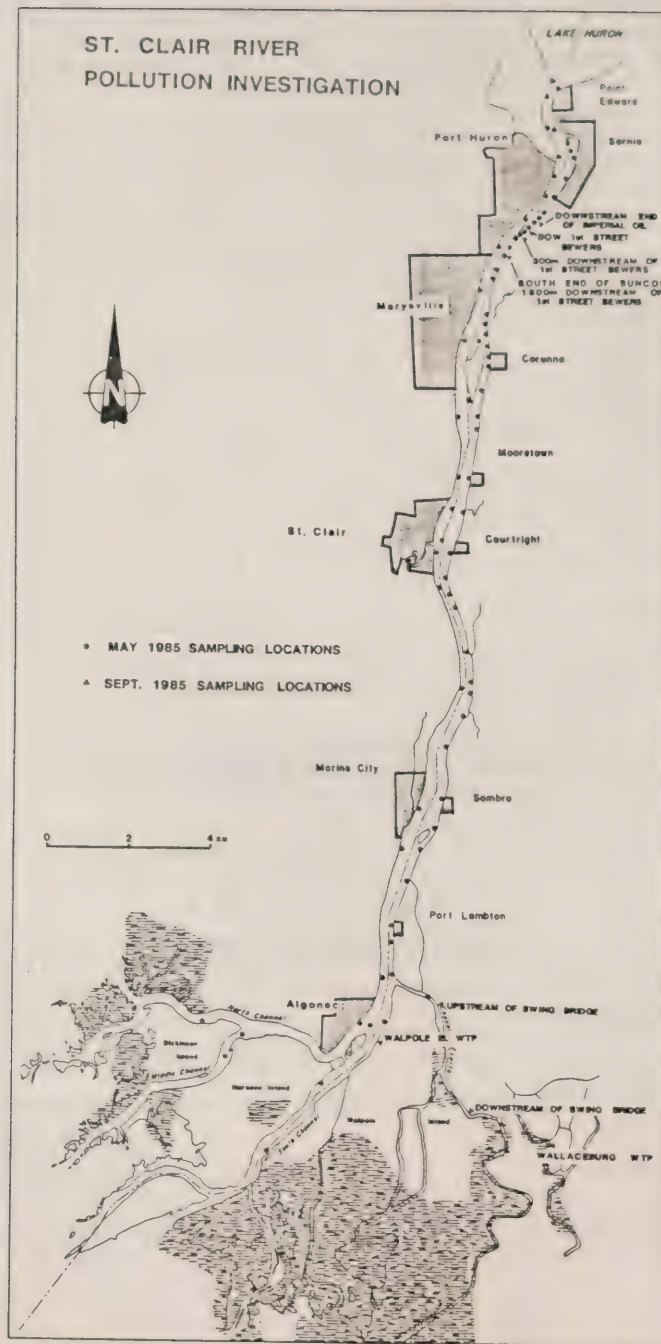


Figure 3.23 1985 MOE St. Clair River sampling locations.

PERCHLOROETHYLENE IN WATER--SEPT. 1985

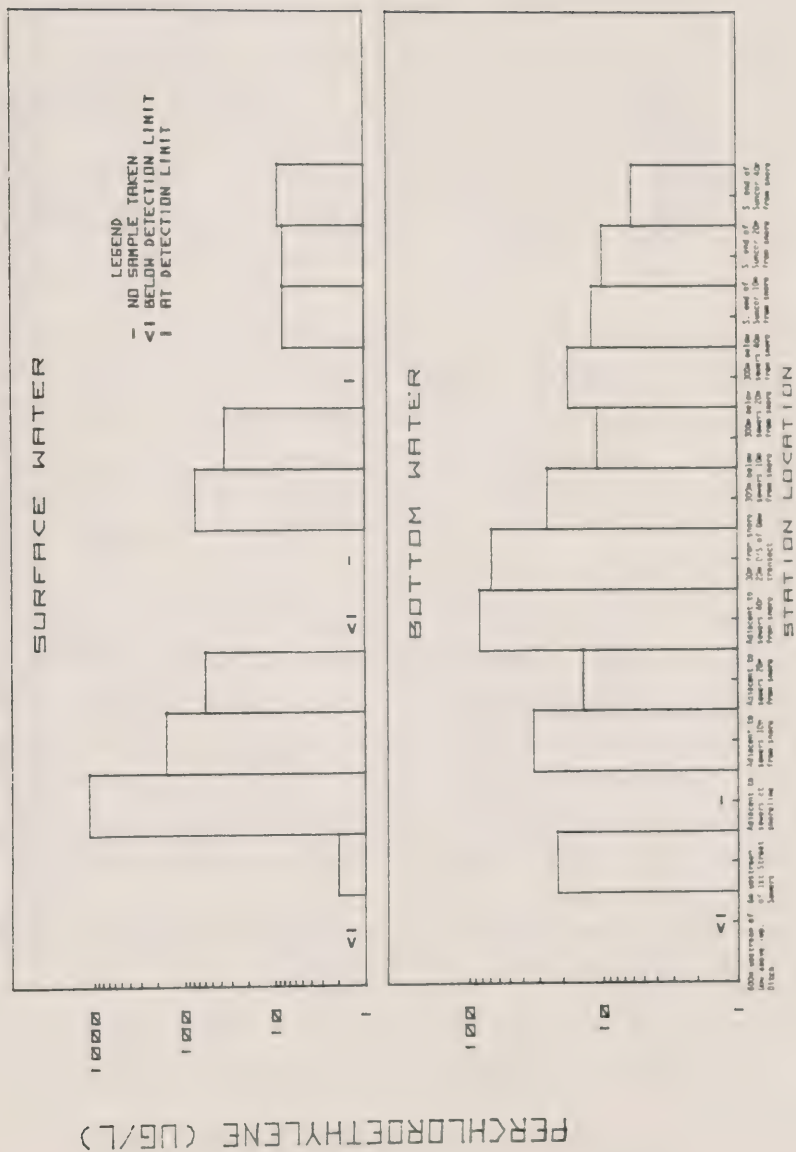


Figure 3.24 Perchloroethylene in water, September 1985.

CARBONTETRACHLORIDE IN WATER--1985

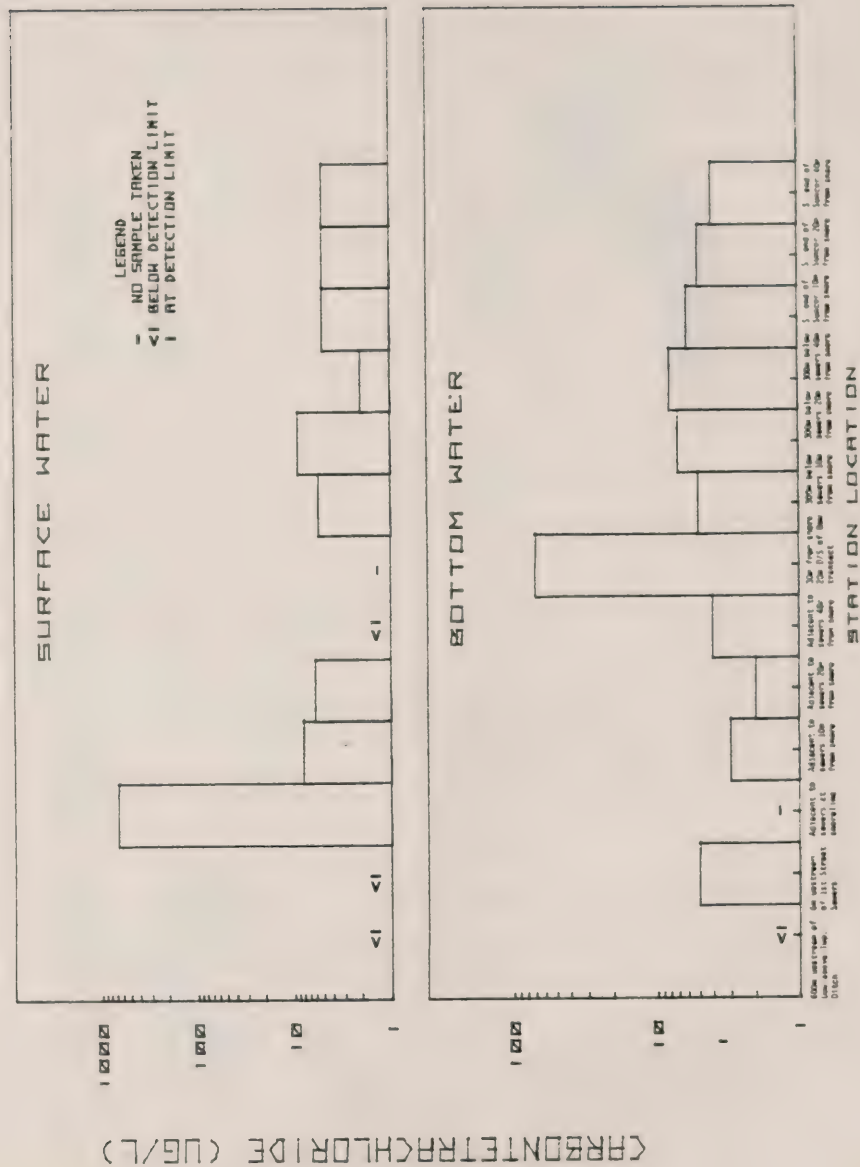


Figure 3.25 Carbon tetrachloride in water, 1985.

The declining trend of surface levels with distance offshore, coupled with increased bottom concentrations, was also observed at a transect 300 m downstream from Dow's 1st Street sewers. At 40 m offshore on this transect a bottom concentration of 18 $\mu\text{g/L}$ was observed, whereas 1 $\mu\text{g/L}$ was noted at the surface. However, at the southern boundary of Suncor levels approached the ambient criterion.

Carbon tetrachloride exhibited a pattern similar to that of tetrachloroethylene. At the southern end of Suncor uniform distribution of both contaminants in the water column was observed. Levels of carbon tetrachloride exceeded the U.S. EPA ambient water quality criterion only in the vicinity of Dow 1st Street sewers.

The pattern of concentration distributions for perchloroethylene and carbon tetrachloride observed during the September survey suggests effects of continuous discharges from point sources as well as from the puddles on the river bottom. Discharges from shore-based point sources resulted in higher concentrations in surface waters in the near shore areas relative to offshore locations whereas the puddles on the river bottom may have contributed to elevated levels in the offshore bottom water. Although carbon tetrachloride constituted a minor component in the puddles collected in September, its high solubility (800 mg/L at 20°C) may have resulted in the observed concentrations in the offshore bottom waters.

Volatile compounds such as 1,1-dichloroethylene, dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane were detected mainly in the surface waters indicating that discharges from point sources (1st Street sewer) are the major contributors of these compounds.

Chenal Ecarte Depressions

To address the concern that deep depressions in the Chenal Ecarte region might be contributing contaminated ground water to the St. Clair River, bottom water samples were collected from two depressions by both agencies (Fig. 3.21). Surface water samples were also collected from sites just upstream for reference purposes.

Samples were analyzed for volatile compounds as well as carbonate analysis. There were no differences in organic components between samples from the depression area and those from the nearby upstream surface water. Results of carbonate analysis infer that no ground-water seepage is occurring at either location. This information suggests but does not prove that these two holes are not major sources of ground water.

DRINKING WATER SUPPLIES

The Ministry of the Environment has carried out three St. Clair River Area drinking water testing programs (MOE, 1985).

Perchloroethylene Program

This was initiated as a direct result of the August 1985 Dow Chemical spill. Eight St. Clair River area water treatment plants were monitored on a daily basis from the end of August until the end of September. The MOE laboratory's detection limit for perchlorethylene is 1 ppb. During this monitoring, the highest level of perchlorethylene detected in treated drinking

water was four (4) parts per billion (ppb). The World Health Organizations's tentative guideline for perchloroethylene in treated drinking water is 10 ppb.

Monitoring indicated that perchloroethylene levels steadily decreased in the river since the spill (Table 3.7). Twice daily monitoring for perchloroethylene was instituted at Walpole Island and Wallaceburg on November 14, 1985, when the clean-up of material from the riverbed was initiated. Marysville (Michigan) is being sampled once per day. To date, no levels have exceeded one part per billion (ppb) in any sample.

Dioxin Program

MOE has tested for dioxins at four St. Clair area water treatment plants, including Sarnia (Lambton), Wallaceburg, Windsor and Amherstburg, since June of 1985. This program was expanded to include seven area water treatment plants (Sarnia, Walpole Island, Wallaceburg, Amherstburg, Windsor, Mitchell's Bay and Stoney Point) from November 6, 1985. Frequency of sampling was increased from biweekly to approximately weekly after December 16. The average detection limit for various dibenzo-p-dioxin or dibenzofuran congeners in drinking water is 10 parts per quadrillion (ppq). No dibenzo-p-dioxins or dibenzofurans in any form were detected in any treated water samples (Table 3.8).

Dioxins were found in raw water, only in three out of four samples taken from Windsor, and in two samples taken from Amherstburg. However, the forms of dioxins detected were 100 to 10 000 times less toxic than 2,3,7,8-tetrachlorodibenzo-p-dioxin, which was not detected in any sample.

Table 3.7 Perchloroethylene Drinking Water Program

PERCHLOROETHYLENE, ppb				
<u>Facility</u>	<u>Date</u>	<u>Raw</u>	<u>Treated</u>	<u>Remarks</u>
Stag Island (approximately 5 km downstream of Dow Chemical)	Aug. 30	ND	ND	grab samples
	Aug. 31	ND	ND	grab samples
	Sept. 1	ND	ND	grab samples
	Sept. 3	ND	ND	
Walpole Island	Aug. 29	7	-	grab samples
	Aug. 30	2	2	grab samples
	Aug. 31	2	4	composite (2 grabs)
	Sept. 1	2	3	grab samples
	Sept. 2	2	2	
	Sept. 3	2	2	
	Sept. 4	1.4	1.9	
	Sept. 4	0.587	0.891	Dow's samples
	Sept. 5	1.3	1.4	
	Sept. 6	2	2	
	Sept. 7	1.4	2	
		2	2	
	Sept. 8	-	-	
	Sept. 9	1.4	2	
	Sept. 17	1.0	1.0	
	Nov. 6	ND	ND	DWSP samples
	Nov. 14	ND	ND	2/day grab samples
	Nov. 15	ND	ND	2/day grab samples
	Nov. 15	ND	ND	DWSP samples
	Nov. 16	ND	ND	2/day grab samples
	Nov. 17	ND	ND	2/day grab samples
	Nov. 18	ND	ND	2/day grab samples
	Nov. 19	ND	ND	2/day grab samples
	Nov. 20	ND	ND	2/day grab samples
	Nov. 21	ND	ND	2/day grab samples
	Nov. 22	ND	ND	2/day grab samples
	Nov. 23	ND	ND	2/day grab samples
	Nov. 24	ND	ND	2/day grab samples
	Nov. 25	ND	ND	2/day grab samples
	Nov. 25	ND	ND	DWSP samples
	Nov. 26	ND	ND	2/day grab samples
	Nov. 27	ND	ND	2/day grab samples
	Nov. 28	ND	ND	2/day grab samples
	Nov. 29	ND	ND	2/day grab samples
	Nov. 30	ND	ND	2/day grab samples

Table 3.7 Continued

PERCHLOROETHYLENE, ppb					
Facility	Date	Raw	Treated	Remarks	
Walpole (cont'd)	Dec. 1	ND	ND	2/day grab samples	
	Dec. 2	ND	ND	2/day grab samples	
	Dec. 3	ND	ND	2/day grab samples	
	Dec. 4	ND	ND	2/day grab samples	
	Dec. 5	ND	ND	2/day grab samples	
	Dec. 6	ND	ND	2/day grab samples	
	Dec. 7	ND	ND	2/day grab samples	
	Dec. 8	ND	ND	2/day grab samples	
	Dec. 9	ND	ND	2/day grab samples	
	Dec. 9	ND	ND	DWSP samples	
	Dec. 10	ND	ND	2/day grab samples	
Wallaceburg	June 5	ND	ND	DWSP samples	
	July 3	ND	ND	DWSP samples	
	Aug. 29	7	-		
	Aug. 39	2	3	grab samples	
	Aug. 31	3	4	composite (3 grabs)	
	Sept. 1	3	4	grab samples	
	Sept. 2	3	3	grab samples	
	Sept. 3	2	2		
	Sept. 4	2	2		
	Sept. 4	0.904	0.922	Dow's samples	
	Sept. 5	2	2		
	Sept. 6	3	2		
	Sept. 7	1.2	2		
		2	2		
	Sept. 8	2	3		
	Sept. 9	1.0	1.4		
	Sept. 17	1.0	1.0		
	Oct. 7	ND	ND	DWSP samples	
	Nov. 5	ND	ND	DWSP samples	
	Nov. 14	ND	ND	2/day grab samples	
	Nov. 15	ND	ND	2/day grab samples	
	Nov. 15	ND	ND	DWSP samples	
	Nov. 16	ND	ND	2/day grab samples	
	Nov. 17	ND	ND	2/day grab samples	
	Nov. 18	ND	ND	2/day grab samples	
	Nov. 19	ND	ND	2/day grab samples	
	Nov. 20	ND	ND	2/day grab samples	
	Nov. 21	ND	ND	2/day grab samples	

Table 3.7 Continued

PERCHLOROETHYLENE, ppb					
<u>Facility</u>	<u>Date</u>	<u>Raw</u>	<u>Treated</u>	<u>Remarks</u>	
Wallaceburg (cont'd)	Nov. 22	ND	ND	2/day grab samples	
	Nov. 23	ND	ND	2/day grab samples	
	Nov. 24	ND	ND	2/day grab samples	
	Nov. 25	ND	ND	2/day grab samples	
	Nov. 26	ND	+	DWSP samples	
	Nov. 26	ND	ND	2/day grab samples	
	Nov. 27	ND	ND	2/day grab samples	
	Nov. 28	ND	ND	2/day grab samples	
	Nov. 29	ND	ND	2/day grab samples	
	Nov. 30	ND	ND	2/day grab samples	
	Dec. 1	ND	ND	2/day grab samples	
	Dec. 2	ND	ND	2/day grab samples	
	Dec. 2	ND	ND	DWSP samples	
	Dec. 3	ND	ND	2/day grab samples	
	Dec. 4	ND	ND	2/day grab samples	
	Dec. 5	ND	ND	2/day grab samples	
	Dec. 6	ND	ND	2/day grab samples	
	Dec. 7	ND	ND	2/day grab samples	
	Dec. 8	ND	ND	2/day grab samples	
	Dec. 9	AI	AI	DWSP samples	
	Dec. 10	ND	ND	2/day grab samples	
Mitchell's Bay	May 23	ND	ND	DWSP samples	
	June 18	ND	ND	DWSP samples	
	July 22	ND	ND	DWSP samples	
	Aug. 30	ND	ND	grab samples	
	Aug. 31	ND	ND	grab samples	
	Sept. 3	ND	ND		
	Sept. 4	ND	ND		
	Oct. 7	ND	ND	DWSP samples	
	Nov. 5	ND	ND	DWSP samples	
	Nov. 15	ND	ND	DWSP samples	
	Nov. 25	ND	ND	DWSP samples	
	Dec. 9	AI	AI	DWSP samples	
Tilbury North	Sept. 2	ND	ND	grab samples	
	Sept. 3	ND	ND		
	Oct. 8	ND	ND	DWSP samples	
	Nov. 5	ND	ND	DWSP samples	
	Dec. 3	AI	AI	DWSP samples	

Table 3.7 Continued

PERCHLOROETHYLENE, ppb				
<u>Facility</u>	<u>Date</u>	<u>Raw</u>	<u>Treated</u>	<u>Remarks</u>
Belle River	Sept. 2	ND	ND	grab samples
	Sept. 3	ND	ND	grab samples
Windsor	July 15	ND	ND	DWSP samples
	Aug. 30	3	3	grab samples
	Aug. 31	2	2	grab samples
	Sept. 1	ND	ND	grab samples
	Sept. 2	ND	ND	grab samples
	Sept. 3	ND	ND	
	Sept. 16	ND	ND	DWSP samples
	Oct. 21	ND	ND	DWSP samples
	Nov. 20	ND	ND	DWSP samples
	Dec. 3	AI	AI	DWSP samples
	Dec. 10	AI	AI	DWSP samples
Amherstburg	May 23	ND	ND	DWSP samples
	Aug. 30	3	3	grab samples
	Aug. 31	2	2	grab samples
	Sept. 1	ND	ND	grab samples
	Sept. 2	ND	ND	grab samples
	Sept. 3	ND	ND	grab samples
	Sept. 4	ND	ND	grab samples
	Sept. 23	ND	ND	DWSP samples
	Oct. 28	ND	ND	DWSP samples
	Nov. 19	ND	ND	DWSP samples
	Nov. 25	ND	ND	DWSP samples
	Dec. 2	AI	AI	DWSP samples
	Dec. 10	AI	AI	DWSP samples

NOTE: Analysis for perchloroethylene continued past the date shown, as part of the Drinking Water Surveillance Program. It will continue to be monitored as one of the DWSP routine parameters.

AI: Analysis in progress.

Table 3.8 Dioxin Drinking Water Survey - Results

[illegible]

Table 3.8 Continued

Location	Sample	Date	Chlorinated Dibenzop-dioxins(ppq)					Chlorinated Dibenzofurans(ppq)					
			2,3,7,8-										
			T4CDD	T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF
Windsor	Raw	07/15/85	ND	40	ND	ND	ND	16	ND	ND	ND	ND	ND
	Treated	07/15/85	-	-	-	-	-	NO DATA	-	-	-	-	-
	Raw	09/25/85	ND	ND	ND	ND	ND	22	ND	ND	ND	ND	ND
	Treated	09/25/85	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND
	Raw	10/03/85	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND
	Treated	10/03/85	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND
	Raw	11/20/85	*	ND	ND	ND	ND	63	ND	ND	ND	ND	ND
	Treated	11/20/85	*	ND	ND	ND	ND		ND	ND	ND	ND	ND
	Raw	07/02/85	ND	ND	ND	ND	ND	20	ND	ND	ND	ND	ND
	Treated	07/02/85	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND
	Raw	11/19/85	*	ND	ND	ND	ND	115	ND	ND	ND	ND	ND
	Treated	11/19/85	*	ND	ND	ND	ND		ND	ND	ND	ND	ND
Amherstburg	Raw	07/02/85	ND	ND	ND	ND	ND	20	ND	ND	ND	ND	ND
	Treated	07/02/85	ND	ND	ND	ND	ND		ND	ND	ND	ND	ND
	Raw	11/19/85	*	ND	ND	ND	ND	115	ND	ND	ND	ND	ND
	Treated	11/19/85	*	ND	ND	ND	ND		ND	ND	ND	ND	ND

ND - Not Detected at an average detection limit of 10 ppq.

* - Sample contamination, value cannot be determined.

ppq - Parts per quadrillion, picograms per litre (pg/L).

Conventional water treatment will remove dioxins from the treated water, because dioxins have an affinity for clinging to particulate matter, which is easily filtered from the water during the treatment process in place.

Drinking Water Surveillance Program

Environment Ontario's regular Drinking Water Surveillance Program at the seven area water treatment plants monitored approximately 140 parameters, including 64 organic compounds. The plants were sampled according to the following schedule:

Wallaceburg	June 5, July 3, August 5, September 3, October 7, November 5, 15, 26, December 2, 9
Mitchell's Bay	June 18, July 23, August 26, September 23, October 28, November 25, December 9
Windsor	July 15, August 16, September 16, October 21, November 20, December 3, 10
Stoney Point	June 5, July 2, August 6, September 3, October 8, November 5, December 3
Amherstburg	May 23, August 26, September 23, October 28, November 19, December 2, 10
Walpole Island	November 6, 15, 25, December 2, 9
Sarnia	November 15, December 2, 9

The levels of trace metals and inorganic ions found are consistent with those found in treated water supplies throughout the province. Most organic parameters were not detected. Although some organic compounds were found in the raw waters sampled, only five other than trihalomethanes were detected in the treated waters (McCarty, 1985). Of the total organic compounds looked for in the treated water, none were found at levels approaching the Drinking Water Objectives of Ontario or other jurisdictions.

The five that were detected (1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, pentachlorobenzene, benzene, and carbon tetrachloride) were found at levels which indicated their definite presence in treated drinking water, at least on one occasion at one or more locations. These compounds were also found in ambient waters as previously shown in Figure 3.22a and 3.22b.

1,2,4,5-tetrachlorobenzene was found at four locations, on August 26 at Mitchell's Bay at 25 ppt, on November 15 at Sarnia at 12 ppt, on November 21 at both Amherstburg and Windsor at 15 ppt and 35 ppt, respectively. The U.S. Environmental Protection Agency (EPA) has set an "ambient" water guideline (set on the assumption that water and fish are consumed from the same water source over a lifetime) of 38 000 ppt.

On October 8, 1985, 25 ppt of 1,2,3,5-tetrachlorobenzene was detected in treated water at Stoney Point, and on November 15, at 23 ppt at Walpole Island; the EPA 'ambient' water guideline for 1,2,4,5-tetrachlorobenzene is 38 000 ppt and this is the most toxic of the isomers, and should thus provide a substantial margin of safety when applied to the 1,2,3,5-isomer.

On July 15, 1985, pentachlorobenzene was detected at the lowest quantifiable level of 10 ppt in treated water at Windsor; the EPA ambient water guideline for this substance is 74 000 ppt.

Carbon tetrachloride was found on three occasions at Wallaceburg, on June 5, November 5, and November 26, 1985 at a level of 1 ppb and at Walpole Island on November 6 and 25 also at 1 ppb. The World Health Organization (WHO) has set a tentative guideline value of 3 ppb for this compound.

Benzene was detected at 1 ppb on only one occasion in treated water at Walpole Island on November 15, 1985. The WHO has set a guideline value of 10 ppb.

Recommendations

- *The on-going drinking water surveillance phase should be continued at water treatment plants on the St. Clair River.*
- *Drinking water criteria and objectives documents should be developed for compounds of health significance found in the treated drinking water, i.e., 1,2,4,5,-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, pentachlorobenzene, benzene and carbon tetrachloride.*
- *Contingency treatment technology should be developed for use after chemical spills, i.e., mobile treatment units.*

Summary

Independent of the sampling dates, methodologies and detection limits used by the two agencies, the results presented in this section point to a number of identical conclusions. It is evident that a variety of contaminants are present in St. Clair River water downstream from the Sarnia industrial area. In particular, the following compounds have been observed: hexachlorobenzene; hexachlorobutadiene; hexachloroethane; octachlorostyrene; pentachlorobenzene; 1,2,4-trichlorobenzene; 1,2,4,5- and 1,2,3,5-tetrachlorobenzene; perchloroethylene; carbon tetrachloride; chloroform and other haloforms; trichloroethylene; 1,1,1- and 1,1,2-trichloroethane; dichloroethane; 1,1,2,2,-tetrachloroethane; and benzene. In addition, several as yet unidentified products have been found. Most of these compounds are present in several industrial effluents, especially the 1st Street sewer complex at Sarnia. For the volatile chlorocarbons, such as perchloroethylene and carbon tetrachloride, continuous discharges from the 1st Street sewer complex as well as other sources in the Sarnia area are clearly evident. There was no adverse impact on the downstream drinking water supplies.

Due to dilution of the effluents, the contaminant concentrations in water at the mouth of the St. Clair River are several orders of magnitude lower than in the effluents. However, daily loadings of 10 to 100 kg are indicated for several of the contaminants, and the water contamination stretches well into Lake St. Clair, but at parts per trillion levels.

RECOMMENDATION

Water quality objectives for volatile compounds in the St. Clair River should be established as soon as possible.

SEDIMENT SURVEY

Physical Characteristics

The riverbed is cut in hard, stoney glacial clay (the Black Shale Till) in mid-channel and in finer glacial silt-clay (the St. Joseph Till) in its upper banks (Fitzgerald et al., 1979). The tills and their erosion products form much of the bed material. No detailed mapping of the geology of the bottom sediments has been done; the following observations are based largely on inferences from echo-sounding profiles and a small number of samples and direct observations. The sounding records show a hard, irregular bottom in mid-channel and along the base of the shore slopes, which is characteristic of an actively eroding or dredged surface. Bottom material has been interpreted as either exposed glacial till or lag deposits of boulders or gravel eroded from the till by river currents or ship scour. Both bottom types have been noted in diver observations in the north end of the area (Duane, 1967) and underwater television surveys in the south (NWRI, 1985). The bed material observed in both cases was a pavement of well-rounded cobbles and boulders with sand in the interstices.

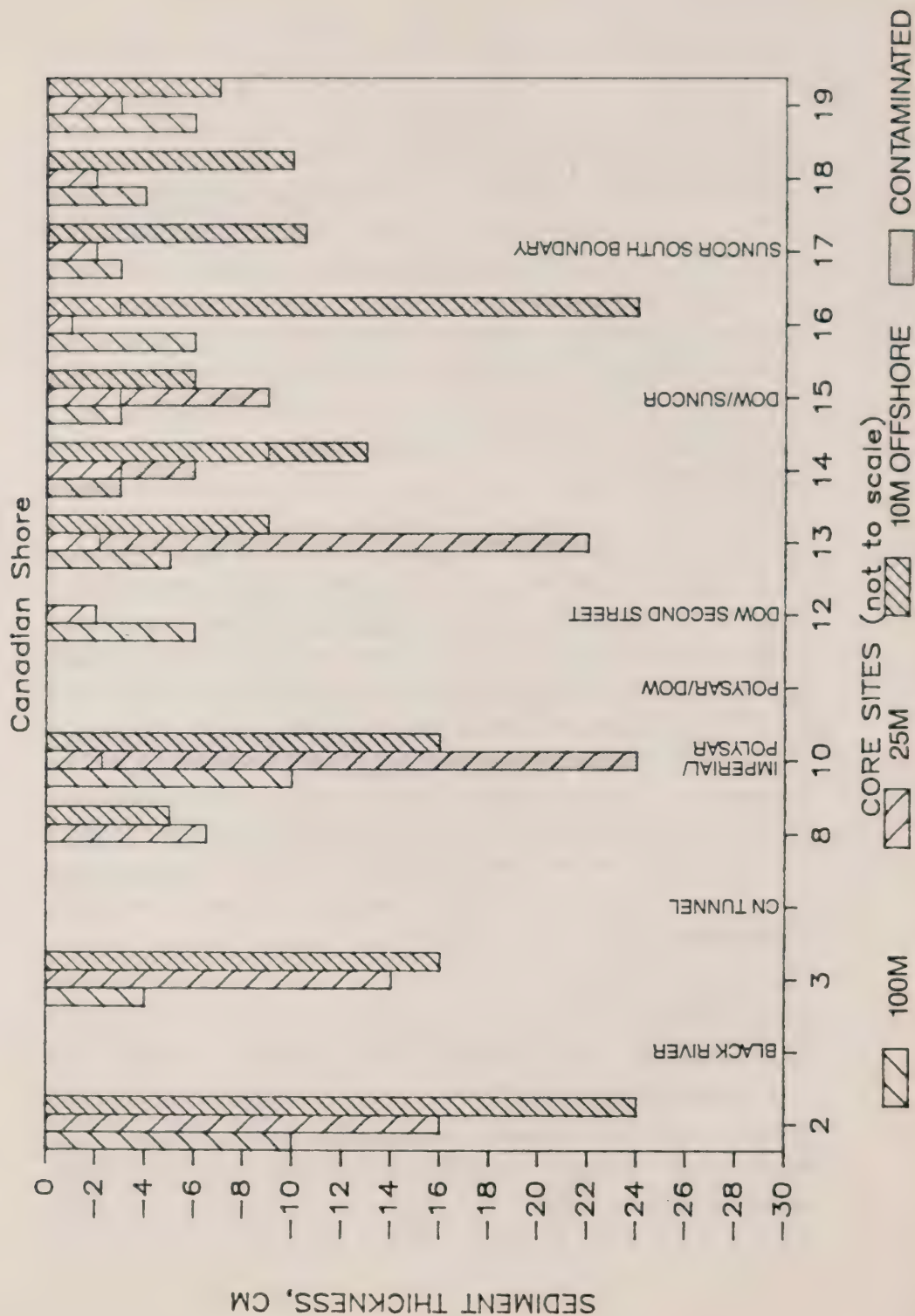
The bottom changes above depths of 7 or 8 m to a more regular, steeper slope with a convex profile. Echo-sounder records of the slope have thin, smooth traces characteristic of sand deposits. Sediment cores collected on the Canadian inshore slope show a sand and gravel cover of variable thickness over cohesive glacial clay, and this is confirmed in diver and television surveys. Data on sediment thickness from cores at 12 sites along the industrial shore (Fig. 3.10) are summarized in Figure 3.26. Values range from 0 to more than 24 cm (longer

cores did not penetrate to the underlying clay) and show no alongshore trends in thickness. Variations in an offshore direction are more systematic and indicate a wedge-shaped deposit that is thickest at the shoreline and pinches out about 100 m offshore. A crude estimate of sediment volume contained in this prism may be obtained by using a simple unweighted average of the thickness values (9 cm) and an assumed deposit width of 100 m. This yields a volume of $63\,000\text{ m}^3$ for the 7-km shore reach extending from the Black River mouth to about 1 km south of the Suncor property.

Figure 3.26 also shows the spatial and vertical distribution of contaminated sediments in the cores. Tarry sediments are first observed just north of the Imperial/Polysar boundary and extend to south of the Suncor property. They occur at the surface or just below the surface (2 to 3 cm) in the cores 10 m and 25 m offshore but are generally absent in the 100-m core. South of the Dow/Suncor boundary, they are present only in the inshore core. Where clean sediment overlies contaminated sediment, there is a sharp, rather than gradational, contact between the two. The cohesion provided by the tar apparently stabilizes the contaminated sediments and prevents or at least slows their incorporation into bedload transport.

RECOMMENDATION

Investigation should be initiated to determine identity and probable sources of sediment contamination that persisted in the deeper layers of cores collected in the vicinity of the Ontario shoreline of the river.



Grain size data for surface sediments from the inshore Canadian slope are summarized in Figure 3.27 and Table 3.9. Two bottom types are represented: fine-grained glacial sediment (the cohesive glacial clay referred to above) and coarser granular deposits (the veneer of mobile river sediments). Data at stations 8 and 14 are representative of the glacial sediments. Clay is the major component, sand is less than 10% and gravel is negligible; mean size is less than 0.008 mm. The river sediments show large variations in grain size from station to station and no consistent pattern of size increase or decrease down river. Average texture is 63% sand, 32% gravel and 5% silt-clay. Mean grain size ranges from 0.1 to 9.0 mm and averages 1.7 mm, but most of the sediment is concentrated in two size modes: 4 to 32 mm (fine gravel) and 0.1 to 0.5 mm (fine-medium sand). No significant vertical variation in grain size with depth below the sediment surface was observed in the several cores for which sub-surface samples were analyzed.

The size data have some implications with respect to the potential sources of the river sediment. The sand mode falls within the size range that is transported by the river as bedload (Duane, 1967) and that is also available from local erosion of the glacial clay. Its presence is consistent with either or both sources. The gravel mode, however, is too coarse for bedload transport or for derivation from the St. Joseph Till as a residual deposit. It is possible that lenses of coarser till or gravel occur within the St. Joseph unit but are not represented in the cores because they are difficult to sample. If this is the case, erosion of these units could account for the presence of gravel. Alternatively, the gravel may be fill used to extend or stabilize the shore slope. Indirect evidence of filling is present in aerial photographs, and it is possible that the

Table 3.9. Grain Size Data, Surface Sediment Samples, 1984-85

Site No.		Pct Gravel	Pct Sand	Pct Silt Clay	Mean Size (mm)
2B		6.7	91.5	1.9	0.28
603		2.9	81.4	15.7	0.11
3B		3.1	94.8	2.1	0.32
6B		71.9	28.1	0	3.7
8B	Glacial	0	7.4	92.6	0.002
604		19.8	78.7	1.5	0.61
10B		3.9	90.0	6.1	0.2
605		63.5	34.9	1.6	2.3
606		13.1	71.8	15.1	0.23
608		5.3	71.7	23.0	0.12
12B		68.5	31.2	0.3	3.7
609		1.2	93.9	4.9	0.17
13B		19.1	80.8	0.1	0.72
610		6.9	81.6	11.5	0.2
14B	Glacial	0	5.0	95.0	0.008
611		7.4	90.8	1.8	0.33
612		60.1	39.5	0.4	2.1
15B		62.9	37.0	0.1	3.2
17B		87.7	12.1	0.2	8.9
19B		71.0	28.9	0.1	3.1

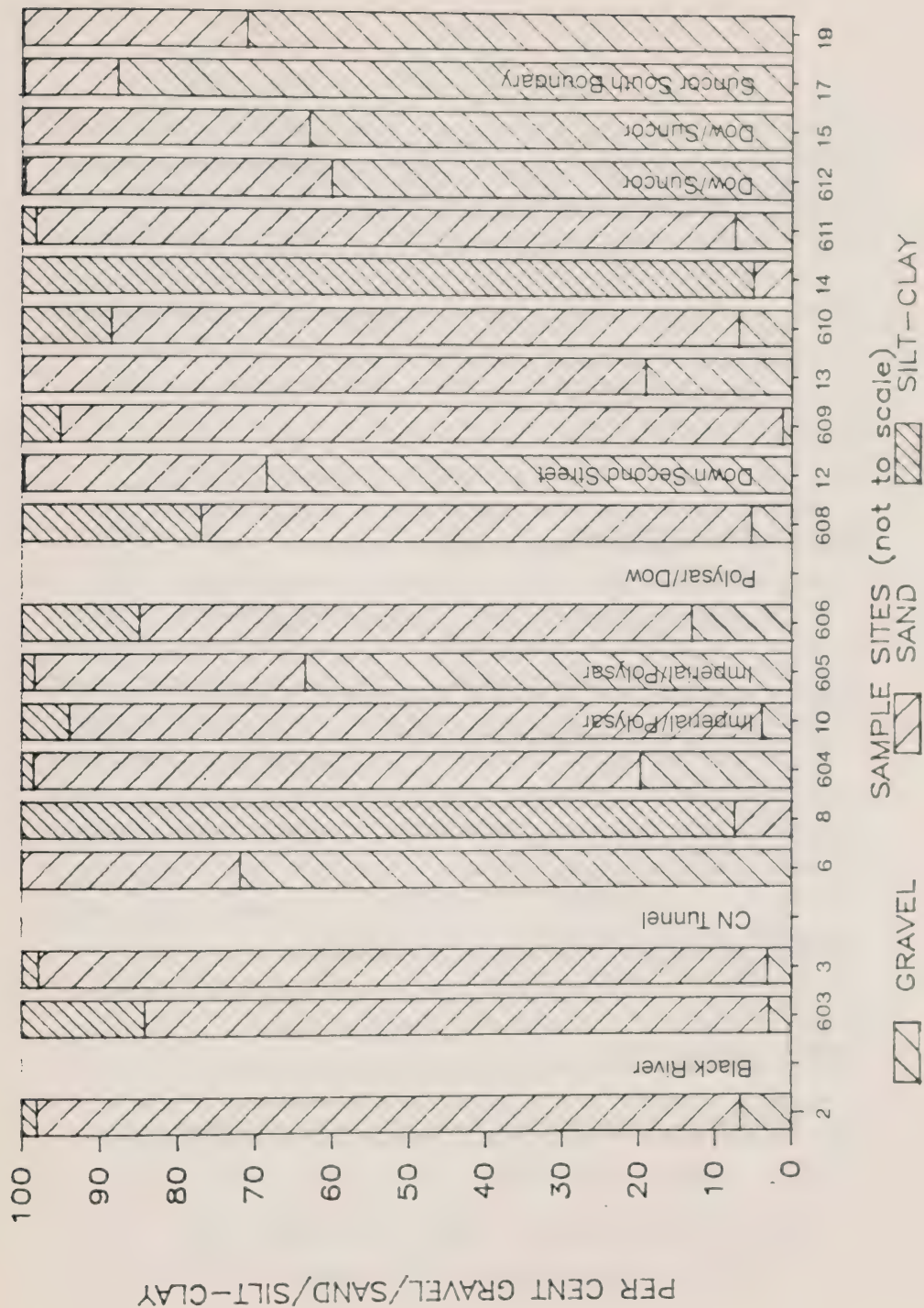


Figure 3.27 St. Clair River bottom sediment grain size.

heterogeneity of grain size and sediment thickness observed in the cores and underwater television footage reflects the presence of fill rather than natural variability. Confirmation of this would require more data on the shore history and sediment stratigraphy and mineralogy than are currently available. For the moment, it should be recognized that some of the slope sediment may be artificial and that its properties will not necessarily reflect the hydraulics of the river or the transport and accumulation rates of bottom sediments.

Chemical Characteristics

This section of the report will discuss sediment surveys conducted by Environment Canada (DOE) in 1985 and 1984 and by the Ministry of the Environment (MOE) in 1985, 1983 and 1977. The samples collected by Environment Canada in 1985 were benthos cores, whereas all other samples of DOE and MOE were surficial sediments collected by divers or with a Shipek dredge. These differences in sampling methodology coupled with slightly different sampling locations mean the results are not exactly comparable. Nevertheless, essentially the same trends and concentrations were observed in both studies.

Sediment Survey (DOE)

The samples described in this report were collected in three phases:

- (1) During the summer of 1984, 45 surficial sediments (top 10 cm) were collected by the Great Lakes Institute of

the University of Windsor along the St. Clair River from Lake Huron to near Russell Island. Thirty-six of these samples were collected from the Canadian side and nine from the U.S. side (Fig. 3.28).

- (2) During the summer of 1985, 160 sediment samples were collected from 20 transect lines on an 8-km reach of the river south of Sarnia. Three samples were collected along each transect 10, 25 and 100 m from shore. Shallow sediment cores were collected where the Benthos Corer could penetrate to the clay overburden and at other locations Shipek grab samples were taken. Geographical locations of the sampling sites for the fall investigation are shown in Figure 3.10.
- (3) During the summer and fall of 1985 suspended sediment samples were collected from Lake St. Clair using sediment traps.

Analysis

Sectioned or total bottom sediments and suspended sediment samples were analyzed for a broad spectrum of chlorinated hydrocarbons: 11 chlorobenzenes (from dichloro- to hexachloro-); three chlorotoluenes (2,4,5- and 2,3,6-trichloro and pentachlorotoluene); hexachloroethane; hexachlorobutadiene; octachlorostyrene; the pesticides alpha and gamma benzenehexachloride, gamma chlordane, mirex and pp'-DDE, pp'-DDD, pp'-DDT; and polychlorinated biphenyls (PCBs). Each sample was sieved (number 10 mesh, 2 mm exclusion) to remove coarse stones and debris and then homogenized in a blender prior to removal of a representative

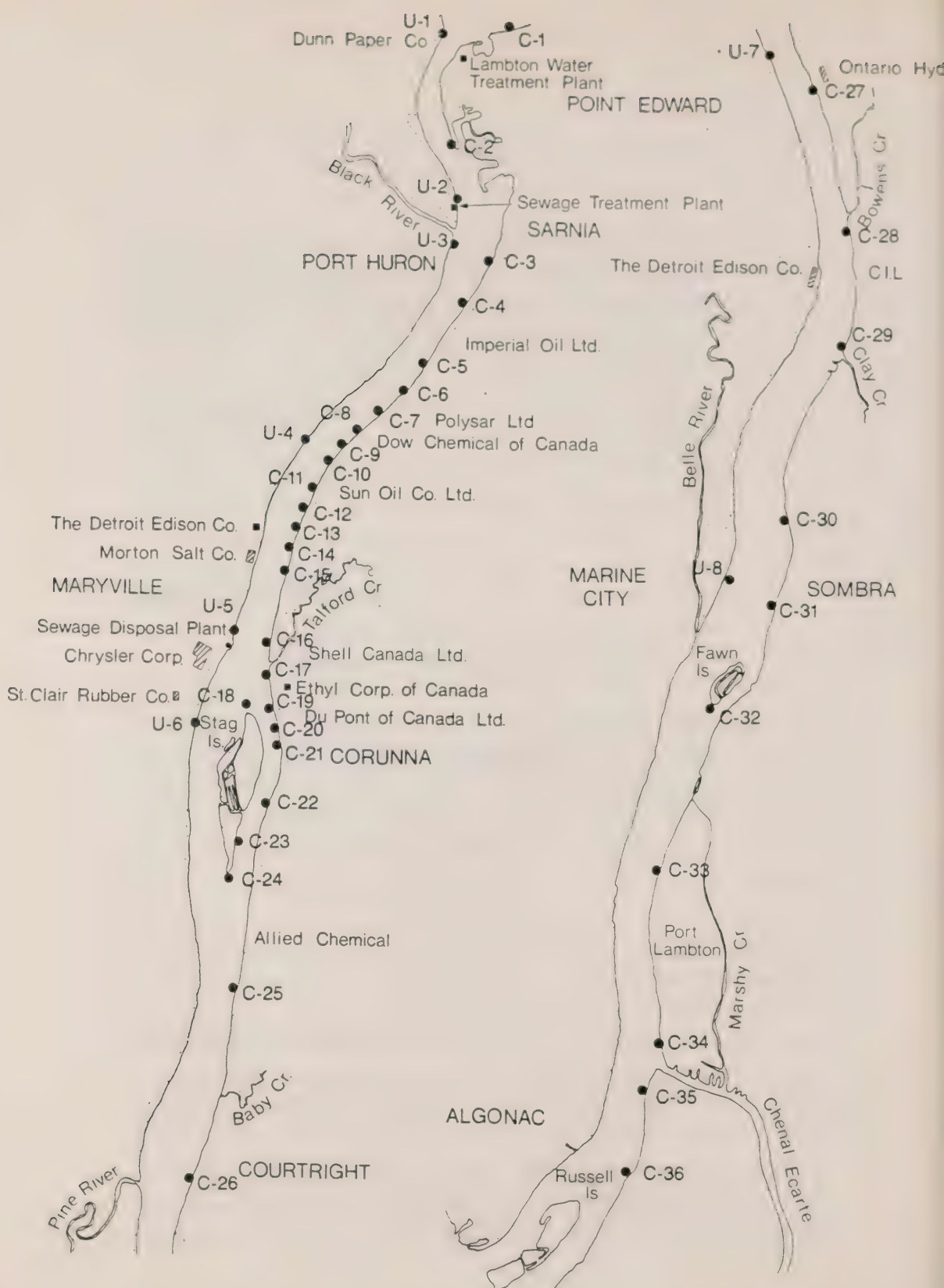


Figure 3.28 Near shore sampling stations, St. Clair River, 1984.

sample. Approximately 20 g net weight (10 g dry weight) of sample was soxhlet extracted for 24 h with 300 mL of a hexane/acetone (41%/59%) mixture. After back extraction of the sample with acidified water to remove the water, the hexane extract was evaporated to 10 mL using a Snyder condenser. The extracts were cleaned up on a $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$ on silica gel/florisil column prior to analysis by gas chromatography. Two capillary columns (30 m) with different polarity phases, DB 5 and DB 17, were used together with electron capture detectors for quantification. Confirmation of chemical identity on selected samples was carried out by capillary gas chromatography/mass spectrometry (GC/MS). This method has been thoroughly tested and provides recoveries greater than 80% for the study chemicals (Oliver and Nicol, 1982).

1984 Data

The sediment samples collected during 1984 from Lake Huron to near Russell Island were analyzed for hexachlorobutadiene, hexachlorobenzene and octachlorostyrene (Table 3.10). These chemicals were present at high concentrations in the tarry material found in the sediments along the industrial waterfront. Mean data for the different stretches of the river are shown in Figure 3.29. There were low to negligible concentrations of the three chemicals at the head of the river and above the CN tunnel, but the values increased dramatically south of the tunnel. The concentrations continued to rise until after the Township ditch (C6), after which there was a slight decline and then a further rise to maximum values offshore from the Dow Chemical Company (in the vicinity of the 1985 perchloroethylene spill). Concentrations remained elevated, although gradually diminishing in

Table 3.10 The Concentration of Hexachlorobutadiene (HCB), Hexachlorobenzene (HCB) and Octachlorostyrene (OCS) in ng/g (ppb) in 1984 Bottom Sediments from the St. Clair River

SITE NUMBER												
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
HCB	ND	ND	0.6	0.3	1300	7200	580	720	1100	940	9600	46000
HCD	ND	ND	4.6	1.3	88	2100	1100	1300	3000	2200	13000	24000
OCS	ND	ND	0.3	0.2	46	1200	530	540	600	1400	1500	4000

SITE NUMBER												
	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24
HCB	320	110	1000	480	79	0.5	140	84	32	280	7.9	3.6
HCD	780	210	2000	390	130	0.4	590	230	62	320	6.9	22
OCS	70	24	490	59	23	ND	88	15	9.3	46	1.2	1.5

SITE NUMBER												
	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	C35	C36
HCB	37	200	150	19	140	450	3.1	71	18	44	41	6.6
HCD	21	1100	1000	35	330	1000	5.3	82	71	130	160	16
OCS	1.2	68	77	6.4	47	230	2.2	12	12	29	35	5.1

SITE NUMBER												
	U1	U2	U3	U4	U5	U6	U7	U8	U9			
HCB	ND	0.2	0.1	0.2	3.7	0.3	0.3	0.8	1.4			
HCD	0.3	1.5	0.4	0.2	3.7	0.5	0.3	0.8	2.8			
OCS	ND	ND	0.1	ND	1.1	ND	ND	ND	ND			

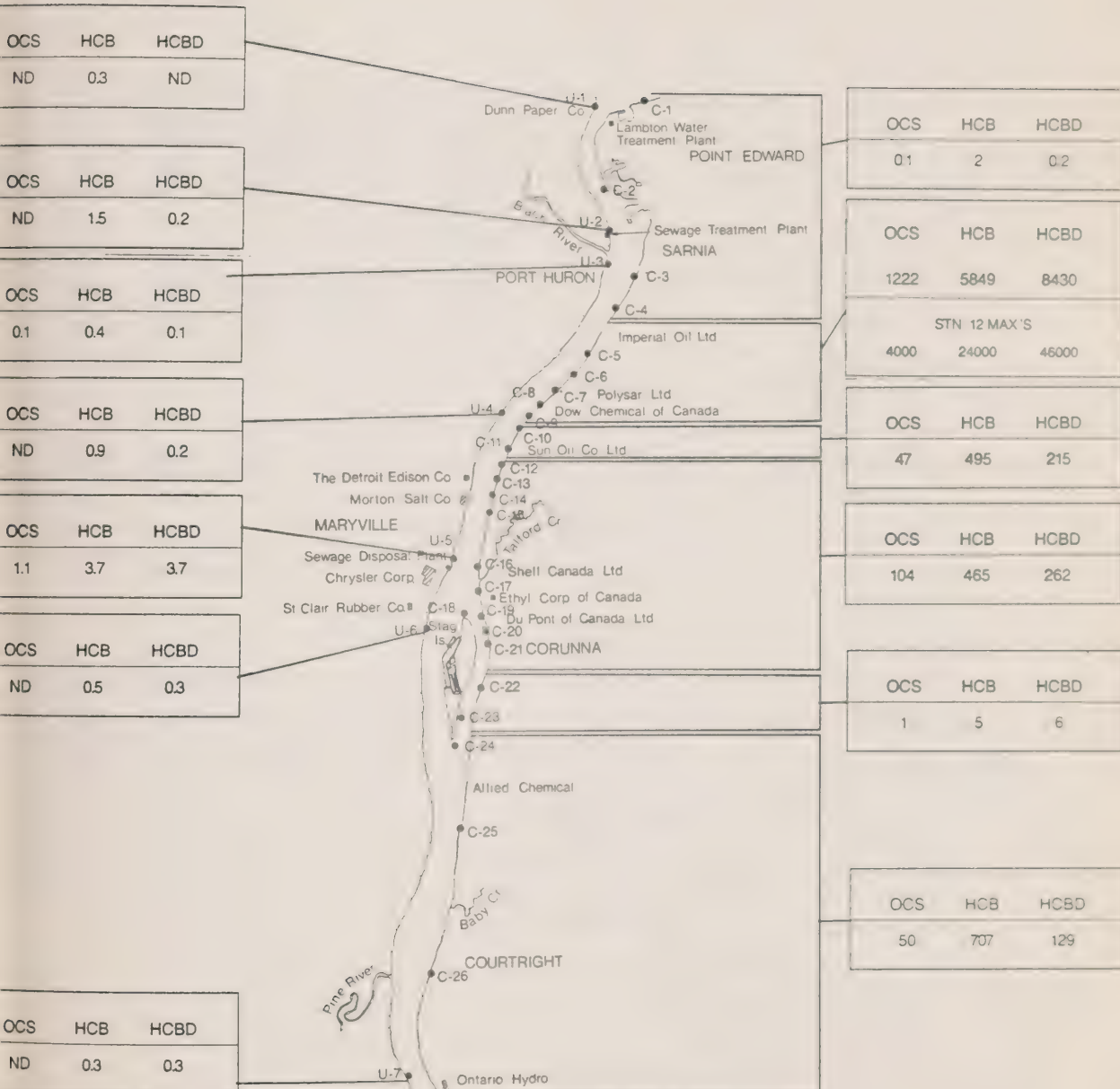


Figure 3.29 Mean concentrations of OCS, HCB and HCB in St. Clair River sediments, 1984.

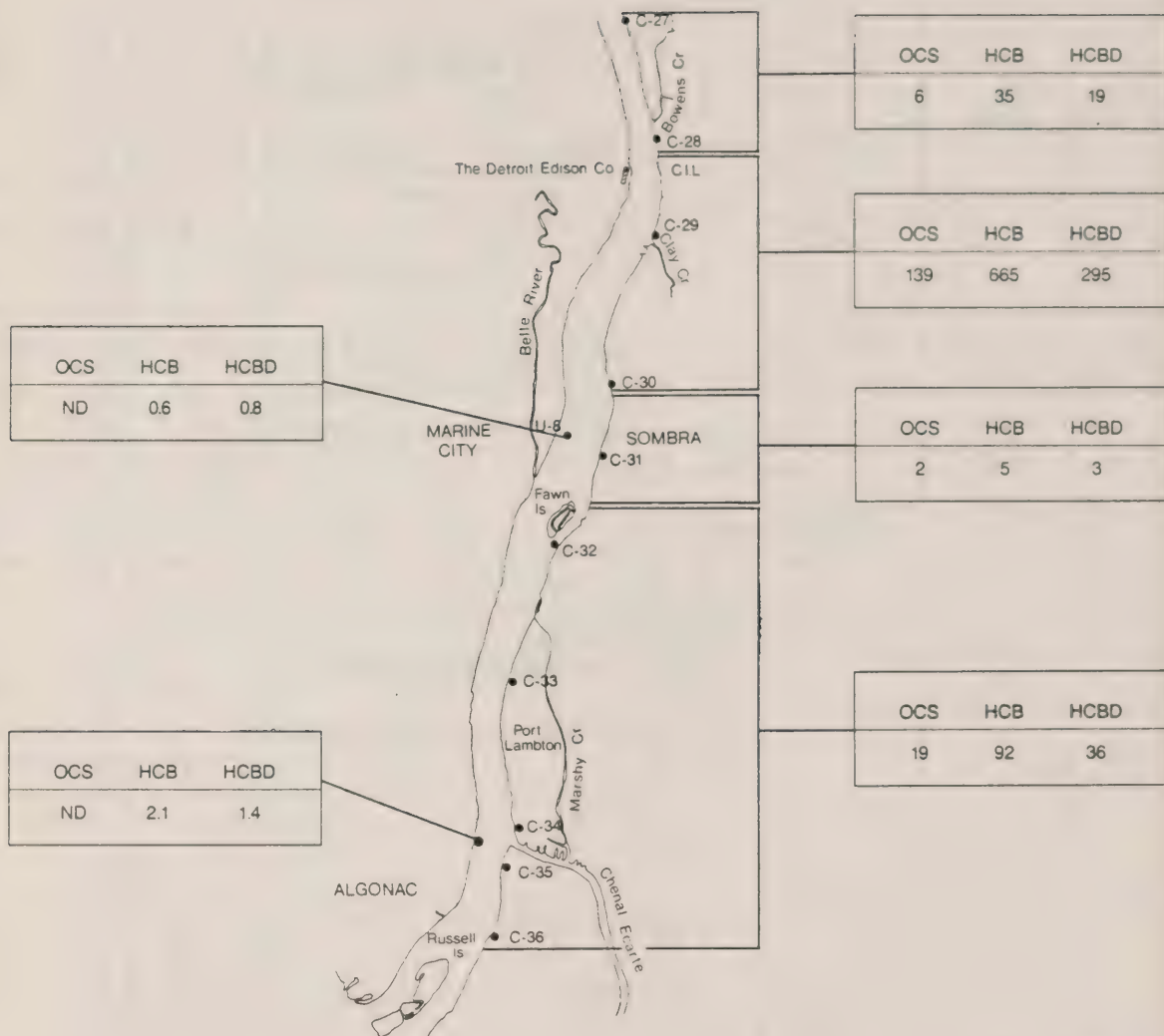


Figure 3.29 Continued.

magnitude, all along the Canadian shore as far as the Delta (Chenal Ecarte). In Figure 3.30, these concentration gradients in the river are illustrated for hexachlorobutadiene.

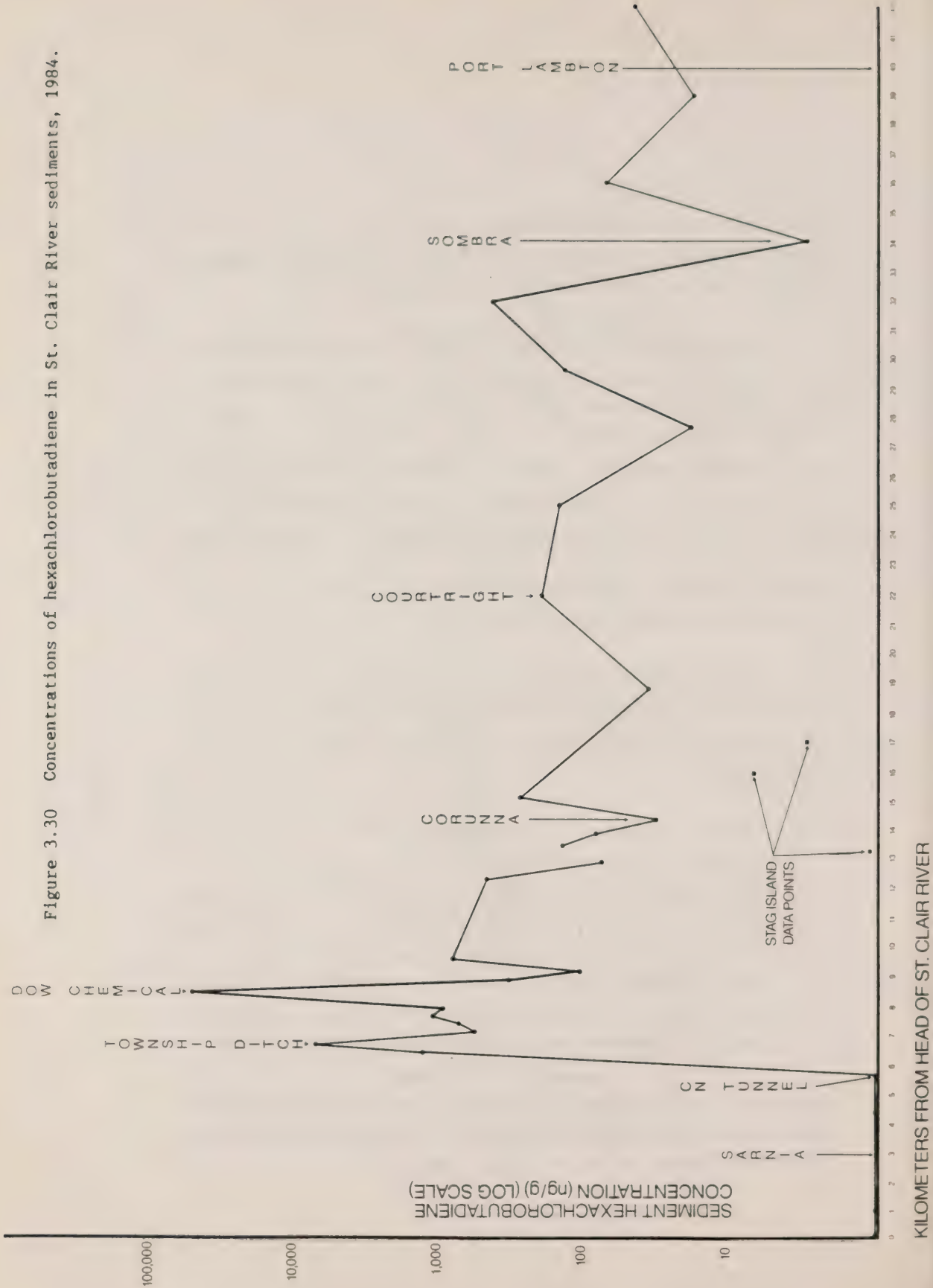
The contaminated sediment appears to have been confined to the Canadian shoreline during 1984. Very low concentrations of these three contaminants were observed at the U.S. sampling locations from Port Huron to Algonac. Low concentrations were also observed near Stag Island for sediment stations which were only about 300 m from the Canadian shoreline (location C18, C23, C24). An aerial photograph taken during May 1947 (Department of Energy Mines and Resources, Ottawa) clearly shows discharge plumes following close to the Canadian shoreline for some considerable distance downstream.

Based on these results, a crude estimate of the total loading of the contaminants in the sediments along the Canadian shore of the St. Clair River can be made using the following approximations:

- Assume a uniform 10 cm layer of sand over the clay for a distance of 100 m from shore.
- Mean concentrations along the 5 km industrial reach near Sarnia. Hexachlorobutadiene - 750 ng/g; hexachlorobenzene - 5200 ng/g; octachlorostyrene - 920 ng/g.
- Mean concentrations for the next 35 km reach of the river of 190 ng/g, 370 ng/g and 48 ng/g for hexachlorobutadiene, hexachlorobenzene and octachlorostyrene, respectively.

These approximations result in a total mass of 79 kg hexachlorobutadiene, 63 kg hexachlorobenzene and 10 kg octachlorostyrene in the 1984 sediments of the St. Clair River.

Figure 3.30 Concentrations of hexachlorobutadiene in St. Clair River sediments, 1984.



In summary, the 1984 sediment data show that significant inputs of hexachlorobutadiene, hexachlorobenzene and octachlorostyrene are entering the river south of the CN tunnel at Sarnia. The largest discharges appear to be in the vicinity of the Township ditch and Dow. The three contaminants studied are major components of the waste products in the production of chlorinated solvents. Dow Chemical Company is the only known producer of chlorinated solvents in the area.

Contaminant Concentrations in Canadian Sediments

The concentrations of several chlorinated contaminants in the Canadian bottom sediment samples are shown in Table 3.11a. The data are presented on bar charts in Figures 3.31 to 3.36 for several key compounds. The chemicals in Table 11a exhibit a wide spectrum of physical and chemical properties. For instance, the volatile compounds such as carbon tetrachloride, trichloroethylene, perchloroethylene and hexachloroethane are not normally found in bottom sediments except close to major point sources. The reason for this is because they have a significant water solubility and are adsorbed only minimally on suspended and bottom sediments. Chemicals such as hexachlorobutadiene, di-, tri- and tetrachlorobenzenes have a somewhat stronger affinity for sediments so are found in significant concentrations in both the water and sediment phases. Compounds such as penta- and hexachlorobenzene, octachlorostyrene and PCBs have a very strong affinity for sediments and so are found mainly in bottom sediments in the aquatic environment. This discussion will be focussed on HCE, HCB, QCD, HCB and OCS compounds which are by products of the production of chlorinated solvents and are found in high concentrations in Dow Chemical effluents and in the

Table 3.11a St. Clair River Bottom Sediment Concentrations
(ng/g or Parts per Billion), November 1995

Compounds	Site 2A	Site 2B	Site 2C	Site 3A	Site 3B	Site 3C	Site 4A	Site 4B	Site 4C	Site 6A	Site 6B	Site 6C	Site 8A	Site 8B	Site 8C	Site 9A	Site 9B	Site 9C
Hexachloroethane	ND	ND	ND	ND	1.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	0.2	1.0	ND
Hexachlorobutadiene	36	0.2	0.6	0.2	1.1	ND	ND	ND	0.3	0.2	0.4	0.8	1.0	0.6	0.7	1.0	4.7	0.6
Pentachlorobenzene	2.2	0.5	0.7	ND	0.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.5	0.9	4.4	0.3
Hexachlorobenzene	6.1	2.1	7.3	0.5	1.5	2.7	2.2	ND	0.8	2.3	1.1	1.5	18	3.1	25	2.1	490	5.7
Octachlorotylene	0.6	0.3	0.2	ND	0.3	0.9	ND	ND	ND	ND	ND	0.3	1.6	0.5	0.7	1.7	12	0.3
Perchloroethylene	2.9	1.8	4.5	1.9	NA	NA	2.1	6.0	2.8	3.0	1.7	1.2	3.6	2.9	5.5	7.9	12	4.8
Trichloroethylene	ND	ND	ND	7.0	NA	NA	ND	ND	ND	ND	5.2	5.2	11	10	ND	ND	ND	ND
Carbon tetrachloride	ND	ND	ND	1.9	NA	NA	ND	ND	ND	ND	ND	ND	8.2	16	12	10	10	10
Dichlorobenzene	130	24	25	ND	6.1	ND	ND	ND	ND	ND	ND	8	74	150	52	34	28	91
Trichlorobenzene	14	ND	2.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1
Tetrachlorobenzene	5.4	ND	0.4	ND	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.2	ND

Sediment Description	Coarse Sand	Coarse Sand	Fine Sand	Stones on Clay	Stones on Clay	Stones on Clay	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand
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NA - Not analyzed.
ND - Not detected.

Table 3.11a. Continued

Compounds	Site 10A	Site 10B	Site 10C	Site 10X	Site 10Y	Site 10Z	Site 11A	Site 11B	Site 12A	Site 12B	Site 12C	Site 13A	Site 13B	Site 13C	Site 14A	Site 14B	Site 14C	Site 15A
Hexachloroethane	15	23	0.4	ND	3.0	1200	29000	16000	550	240	920	290	87	830	21	270	330	22
Hexachlorobutadiene	65,000	67,000	1.2	11	6300	9000	43000	22000	7800	7900	2200	2600	2800	14000	500	7800	16000	540
Pentachlorobenzene	3,500	740	0.4	3.9	1300	9100	12900	4700	410	560	410	210	200	1200	28	1100	560	66
Hexachlorobenzene	7,100	1,100	7.7	24	7200	7200	28000	11000	5100	8900	800	1100	6300	5600	380	73000	2400	1300
Octachlorotylene	6,000	880	0.6	7.2	6200	5200	14000	9200	710	840	76	290	250	280	59	620	350	170
Perchloroethylene	4.2	3,000	7.8	8.1	8.6	420	1400000	250000	420	12000	16000	570	480	1400	NA	600	680	260
Trichloroethylene	ND	320	ND	2.4	3.3	21	110000	4700	42	250	2	56	7	12	NA	37	4.1	19
Carbon tetrachloride	17	ND	12	ND	ND	1.0	630000	20000	15	29	10	7.1	27	8.2	NA	11	3.5	16
Dichlorobenzene	31,000	22,000	40	680	2700	7800	2300	7400	2300	3000	310	12000	18000	34000	5800	2000	200	5200
Trichlorobenzene	1,300	2,400	ND	3.4	980	87	2400	1000	260	22	520	350	2200	2100	250	420	900	160
Tetrachlorobenzene	1,200	300	0.2	1.6	680	720	7000	2000	670	250	230	340	970	1000	65	970	34	140

Sediment Description	Silt & Macrophytes	Gravel & Clay	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand	Gravel & Coarse Sand
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ND - Not Detected.
NA - Not Analyzed.

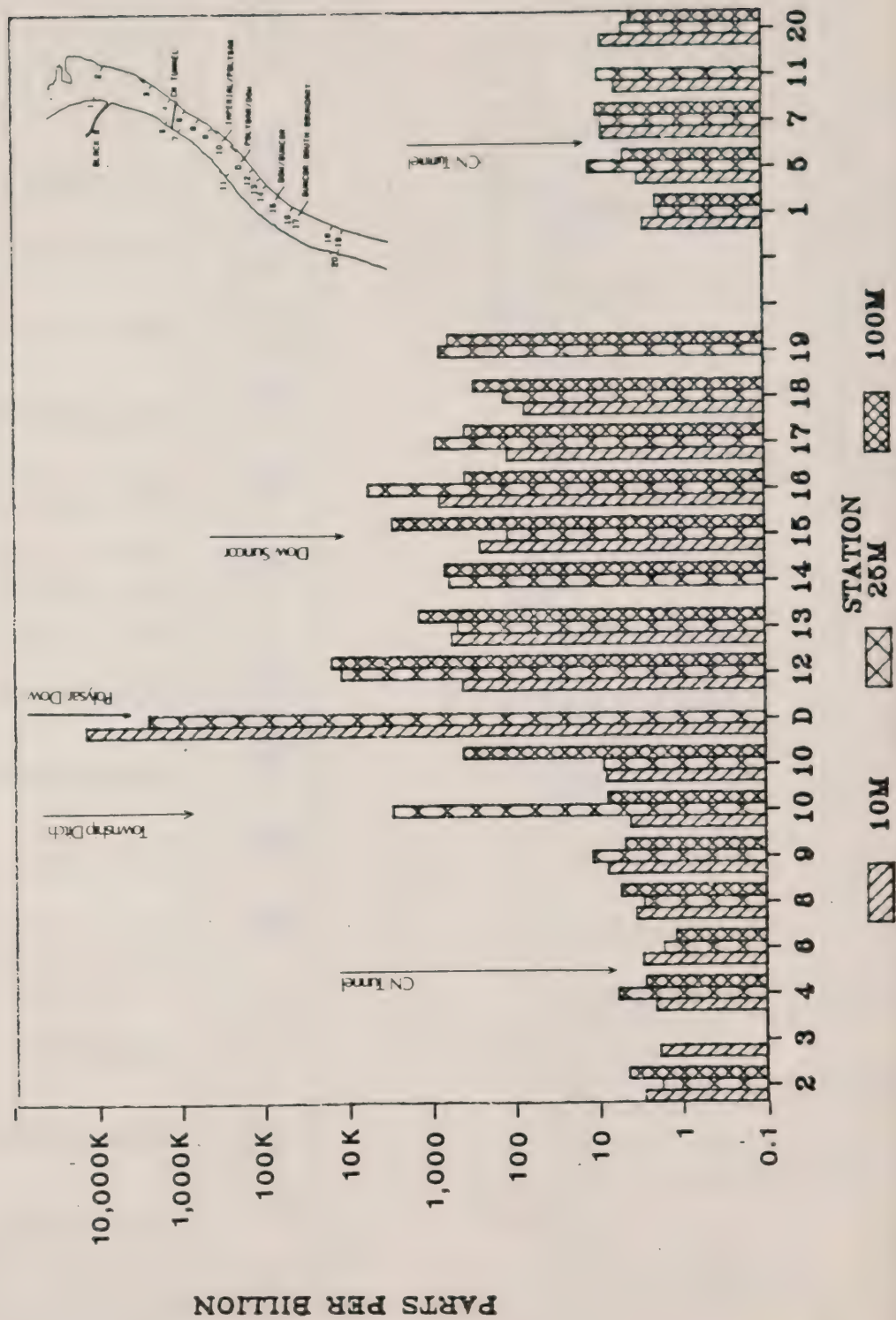
Table 3.11a. Continued

Organic	Site 15B	Site 15C	Site 16A	Site 16B	Site 16C	Site 17A	Site 17B	Site 17C	Site 18A	Site 18B	Site 18C	Site 19A	Site 19B	Site 19C
Hexachlorocyclopentadiene	7	4.9	32	3.9	350	30	16	62	14	6.1	23	0.9	41	100
Hexachlorobenzene	1200	2500	450	930	7300	780	1200	3600	260	2200	720	230	3600	4000
Pentachlorobenzene	79	52	31	52	390	63	26	130	56	67	37	25	93	110
Hexachlorocyclopentadiene	500	300	300	1200	3500	1700	1300	830	3500	1300	220	500	670	570
Octachlorocyclopentadiene	74	93	75	95	190	200	25	220	170	63	66	80	150	83
Pentachlorocyclopentadiene	120	2900	700	5500	390	120	870	390	74	130	300	88	760	600
Trichloroethylene	23	17	32	80	7	25	80	4.3	11	4.5	6.6	88	25	25
Carbon tetrachloride	1.2	80	6	80	9	9	1.6	16	23	1.9	13	88	25	16
Dichlorobenzene	13000	160	5500	550	5100	1100	5200	110	5600	260	210	150	1400	1300
Trichlorobenzene	180	1.6	290	290	720	280	76	21	150	180	10	100	40	38
Tetrachlorobenzene	290	17	57	12	190	110	41	68	57	95	25	48	51	69

MD - Not detected.
MA - Not analyzed.

Table 3.1b. St. Clair River Bottom Sediment Concentrations (ng/g or Parts per Billion), November 1965

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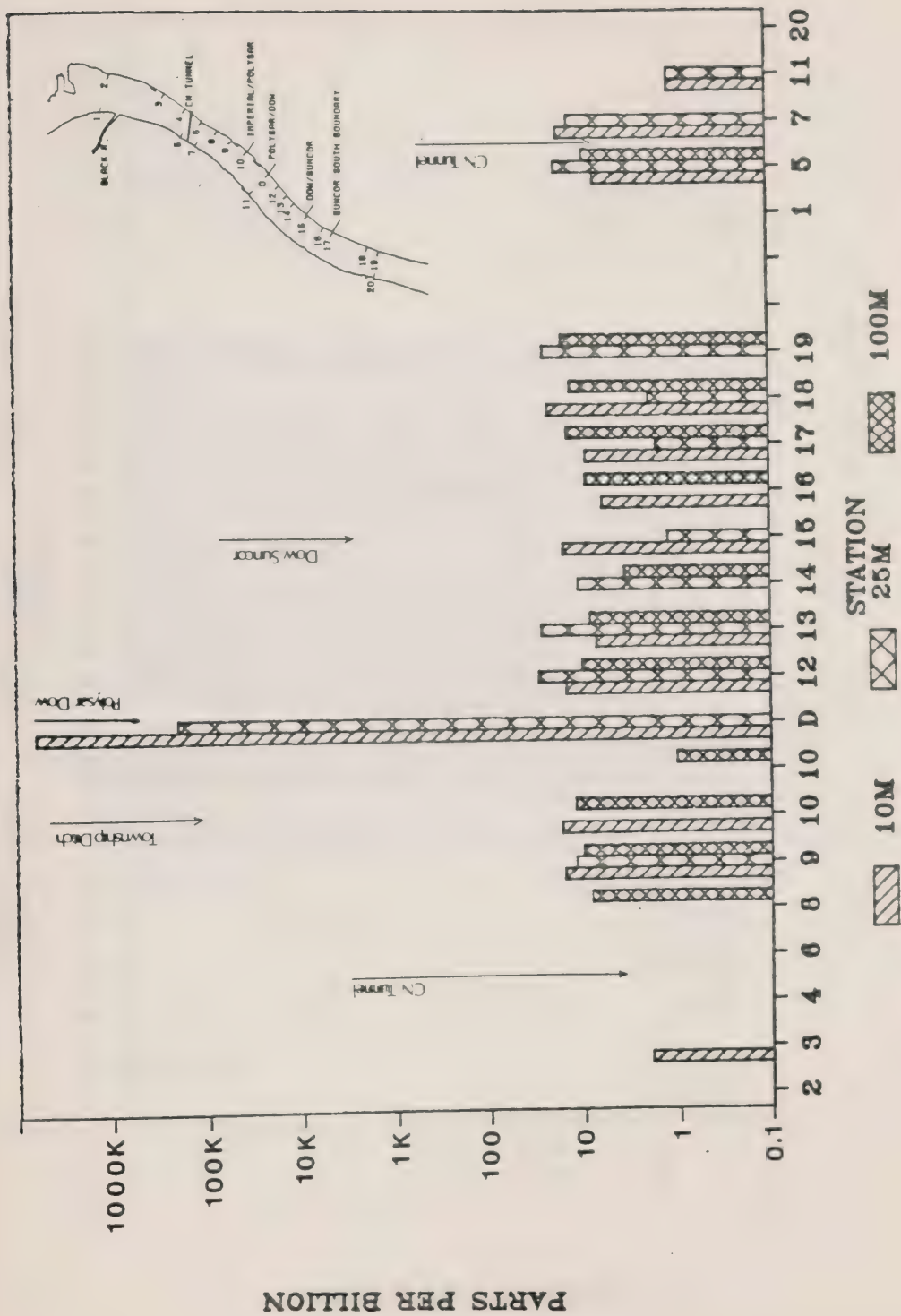


Figure 3.32 Carbon tetrachloride in sediments, St. Clair River, 1985.

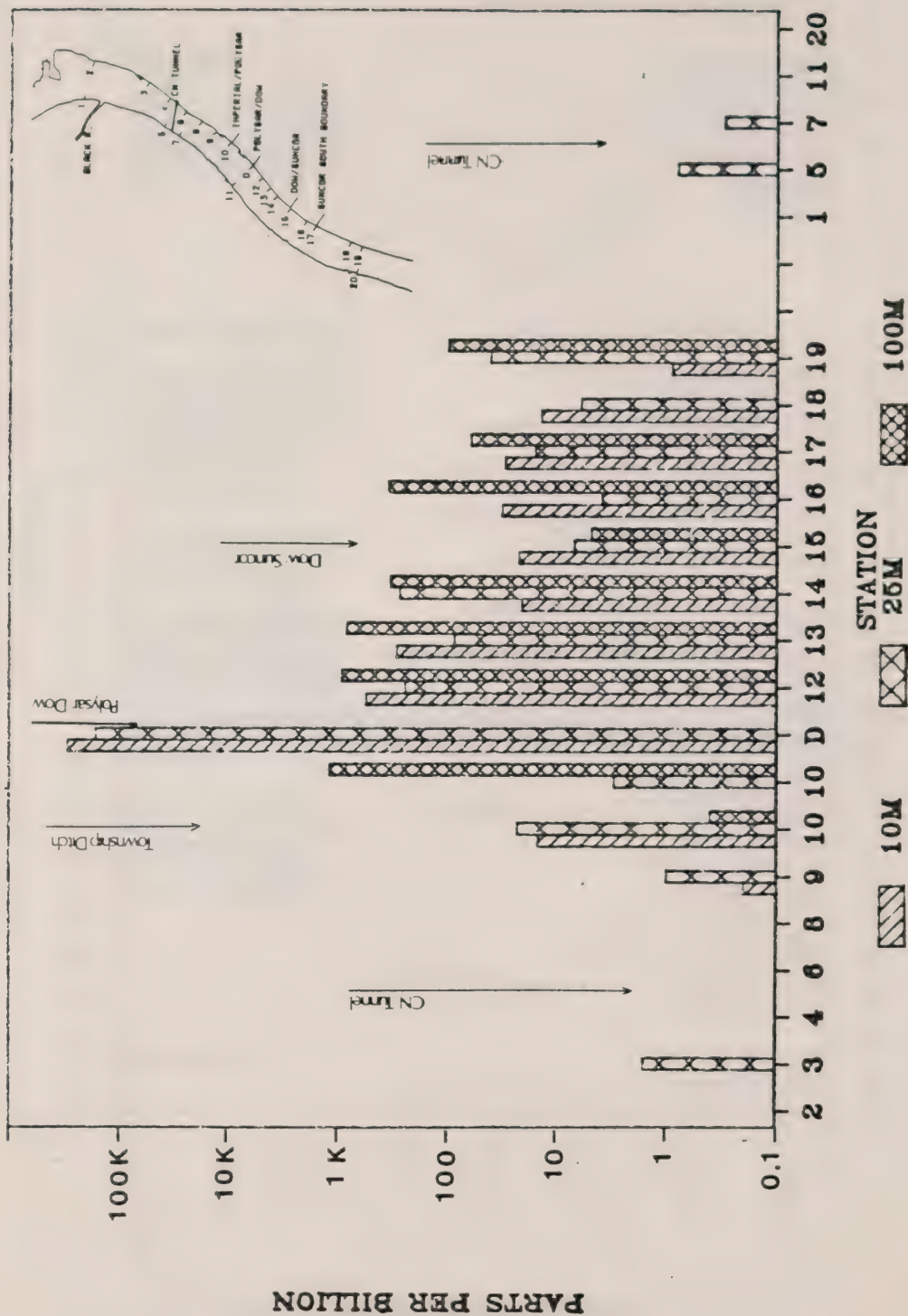


Figure 3.33 Hexachloroethane concentrations in sediments, St. Clair River, 1985.

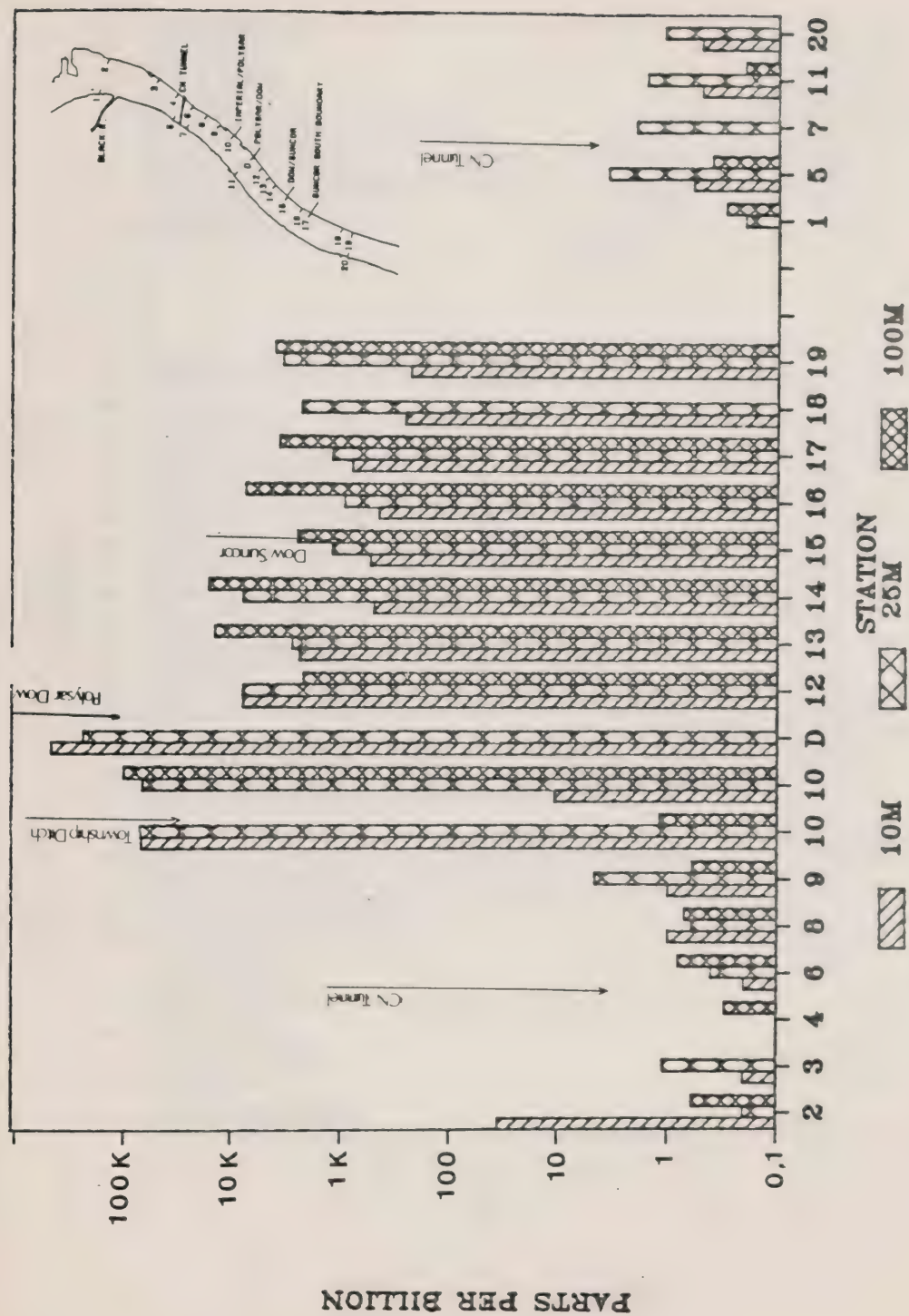


Figure 3.34 Hexachlorobutadiene concentrations in sediments, St. Clair River, 1985.

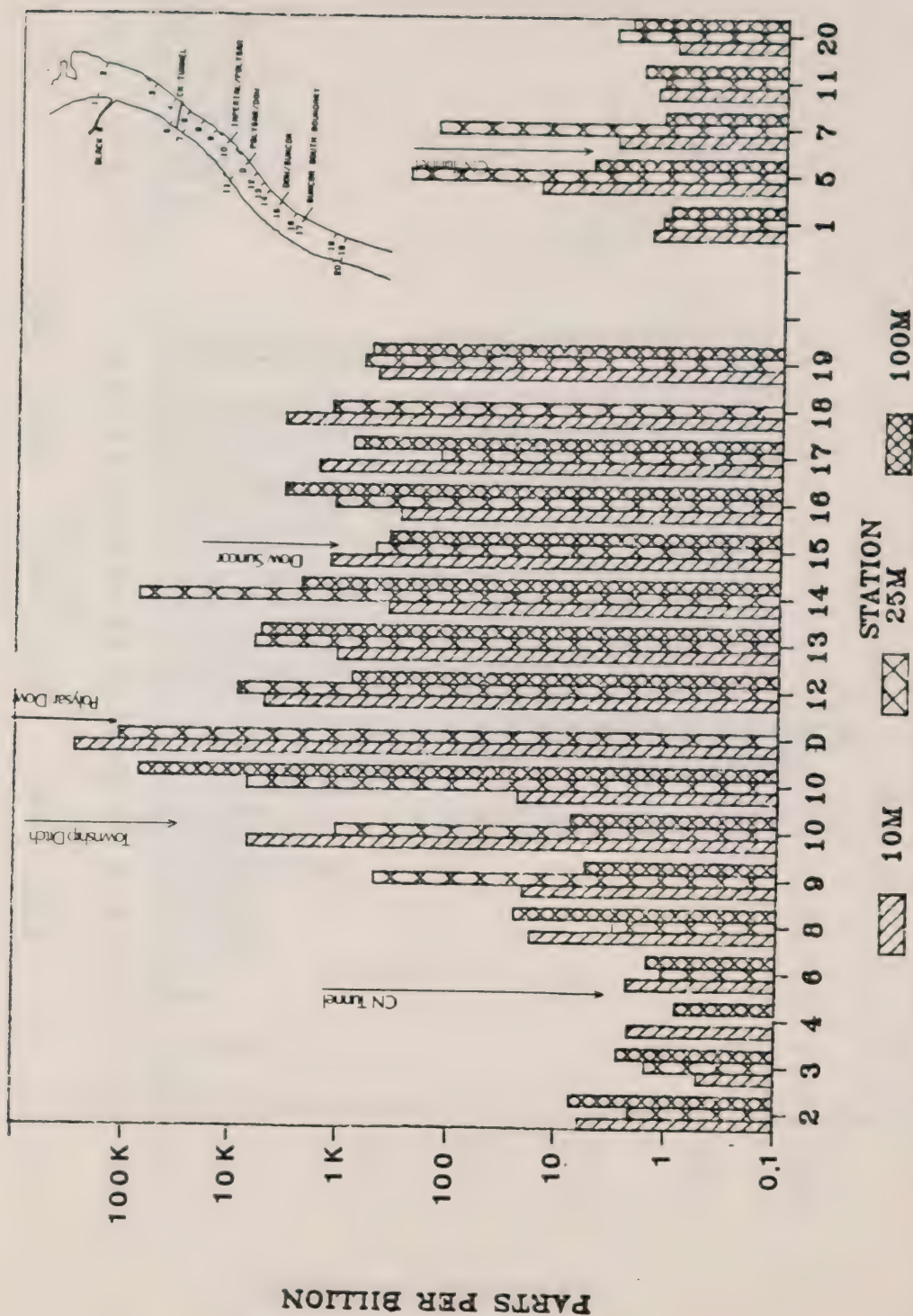


Figure 3.35 Hexachlorobenzene concentrations in sediments, St. Clair River, 1985.

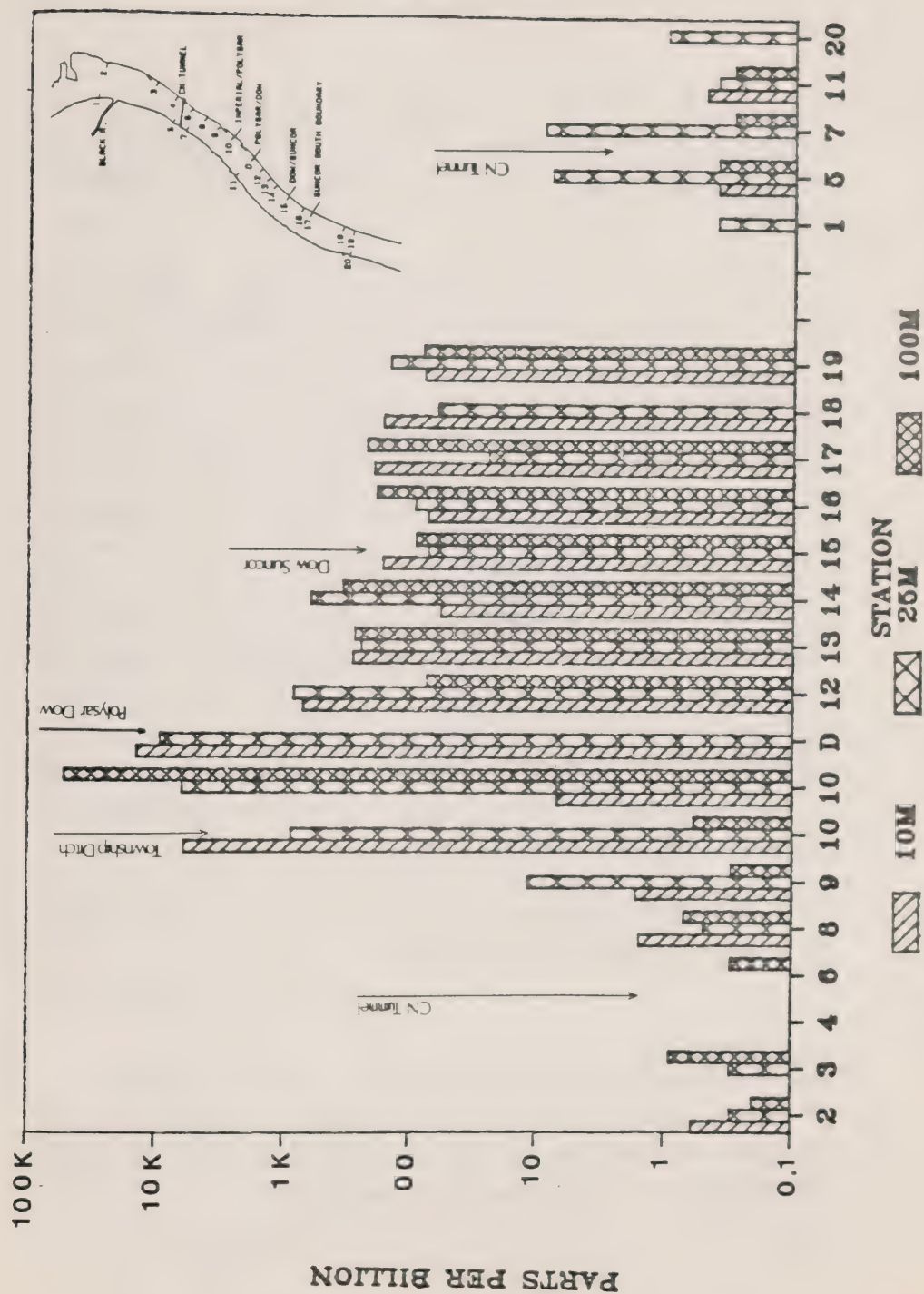


Figure 3.36 Octachlorostyrene concentrations in sediments, St. Clair River, 1985.

St. Clair River perchloroethylene puddles near Dow. Some comments will also be made on the sediment distribution of perchloroethylene, the major constituent of the contaminant puddles.

Low but measurable concentrations of the study chemicals are found at stations upstream from the Sarnia industrial complex. These concentrations reflect widespread, low-level environmental contamination from upstream usage and disposal practices. Along the Canadian shoreline these background levels are recorded up to and including station 6 just below the CN railway tunnel. Concentration increases are observed for several contaminants especially HCB at stations 8 and 9, likely due to inputs from the Sarnia sewage treatment facility as well as urban runoff. Two to three order of magnitude increases for HCB, OCB, HCB and OCS are observed at stations 10A, 10B, 10Y and 10Z. At this location the Township ditch enters the river. This ditch drains the Scott Road landfill site where Dow Chemical has disposed of some of its waste by-products from the production of chlorine and chlorinated solvents. Site 10X is located slightly upstream from the input from the ditch and contains dramatically lower concentrations. Site 10C, 100 m offshore, also has low levels, showing that the ditch plume does not extend out this distance into the river but is swept along the Canadian shoreline.

RECOMMENDATION

The apparent increase in concentrations of hexachlorobenzene in sediments along the Ontario shoreline between the CN tunnel and the Township ditch should be investigated.

Another significant increase or hot spot in concentration is observed where Dow Chemical's 1st Street Sewer discharges into the river. Concentrations for HCE, HCB, OCB and OCS are in the high ppm range at this site. The concentrations of perchloroethylene and carbon tetrachloride at this station are in the percent range. These extremely high sediment concentrations are caused by contamination of the area with the puddles of waste material that have been observed at this location. The two major constituents of these puddles are perchloroethylene and CTC, but they also contain high concentrations of HCE, HCB, OCB, HCB and OCS. All these chemicals have also been observed in Dow effluents and suspended solids from Dow effluents but at much lower concentrations. The very high levels of the volatile constituents perchloroethylene, CTC and HCE in the sediments at this location despite their poor affinity for sediments point to the puddle material as the main source.

The chemical concentrations in the bottom sediments diminish considerably by between one and two orders of magnitude for HCB, OCB, HCB and OCS and by three orders of magnitude for the volatiles perchloroethylene, CTC and HCE at station 12, 300 m below site D. The values are still elevated well above background and remain this way all the way to the end of the station grid - station 19. The 1984 data show that sediment contamination persists to Lake St. Clair.

Although the major chlorinated organics (HCB, OCB, HCB and OCS) are present in all contaminated sediment samples, the ratios of the chemicals do change with source. For example, the ratios HCB/OCS and HCB/OCB are 1.3 and 4.0, respectively, for samples collected near the Township ditch. These ratios are much higher, 16 and 23 respectively, at site D. Stations below site D have

intermediate ratios (HCB/OCS-11; HCB/OCB-17) but closer to site D, indicating that current puddles and Dow effluents have a greater impact on sediment contamination downstream than the Township ditch.

Two sediment cores downstream from Dow at sites 15B and 16A have been analyzed in detail and the results are shown in Table 3.12. With only one exception, HCB in core 15B, the topmost or more recent layer is more contaminated with HCB, QCB, HCB and OCS. Although it is difficult to interpret sediment core data in rivers such as the St. Clair because of the dynamic nature of the sediments, the data appear to indicate recent increasing contamination for these chemicals.

The source and identity of the tarry material which was present at high levels in the sediments for at least 5 km from station 10 to station 19 is not known at present. This material does not seem to be related to the black puddles observed near Dow Chemical. At stations 15B and 16A the sediment depth profile showed that HCB (a major component in the puddles) decreased with depth, while the extractable organics (tarry material) increased with depth in the cores (Table 3.12). This shows that the tarry material and the puddles are not related. Using the mean data for extractable organics in Table 3.12 (500 ppm), it is estimated that there is about 4 metric tons of this tarry material in the sediments from stations 10 to 19. At this time, it is not known how far down the river this contamination extends.

Residues of polychlorinated dibenzo-p-dioxins (PCDD) were measured in sediment extracts from selected river stations and from the Township ditch. Data for the individual homologs are

Table 3.12 The Concentration of HCB_D, QCB, HCB (ppm) and OCS (ppb) and Acetone/Hexane Extractable Organics in St. Clair River Sediment Cores

Sediment Interval (cm)	HCB _D (ppb)	QCB (ppb)	HCB (ppb)	OCS (ppb)	Extractable Organics (ppm)
<u>CORE 16A</u>					
0 - 3	1800	110	1700	210	610
3 - 8	250	17	67	9	510
8 - 13	200	16	54	11	1100
13 - 18	140	24	120	150	670
18 - 24	270	16	110	74	700
END OF CORE					
<u>CORE 15B</u>					
0 - 3	1200	79	500	74	210
3 - 6	1700	51	150	28	400
6 - 9	790	17	78	16	500
CLAY					

given in Table 3.13 and the total PCDD concentrations are shown in Figure 3.37. The limit of detection for 2,3,7,8-TCDD was 3 pg/g (ppt) but was approximately 10 pg/g for OCDD. Low levels of higher chlorinated dioxins were found in samples taken from the Township ditch at Kenny Street and where the ditch enters the river. The total concentrations were 7 ppb in the former sample and 0.6 ppb in the latter. The samples collected at stations D and 2A also contained measurable quantities of dioxins. At the other stations dioxins were either not detected or present at only trace levels. It is important to note that neither the highly toxic 2,3,7,8-TCDD isomer nor the 1,3,6,9-TCDD (associated with 2,4-D formulation) was present in any of the samples.

Contaminants in U.S. Sediments

Much lower concentrations of HCBd, QCB, HCB and OCS were observed on the American side of the river (Table 11b). All stations with the exception of 5B and 7B showed background levels for these contaminants. Stations 5B and 7B, which were located immediately above and just below the CN tunnel, exhibited elevated concentrations for all four contaminants, particularly HCB.

RECOMMENDATION

The apparent increase in concentration of hexachlorobenzene in sediments in the vicinity of the CN tunnel on the Michigan side should be investigated.

Table 3.13. Chlorinated Dibenzo-p-dioxins in St. Clair River Sediments, November 1985

Homologue	Site 2A	Site 5B	Site 6A	Site 7B	Site 8A	Site 9B	Site 10X	Site D	Site 16C	Site 19C	Site 20A
Tetra	ND	ND	ND	ND	ND	ND	ND	0.02	ND	ND	ND
Penta	ND	ND	ND	ND	ND	ND	ND	0.39	ND	ND	ND
Hexa	0.05	ND	ND	ND	ND	ND	ND	0.58	ND	ND	ND
Hepta	0.48	ND	0.08	ND	0.08	ND	0.17	0.56	ND	ND	0.03
Octa	1.10	0.03	0.06	ND	0.10	ND	0.43	ND	ND	ND	0.09

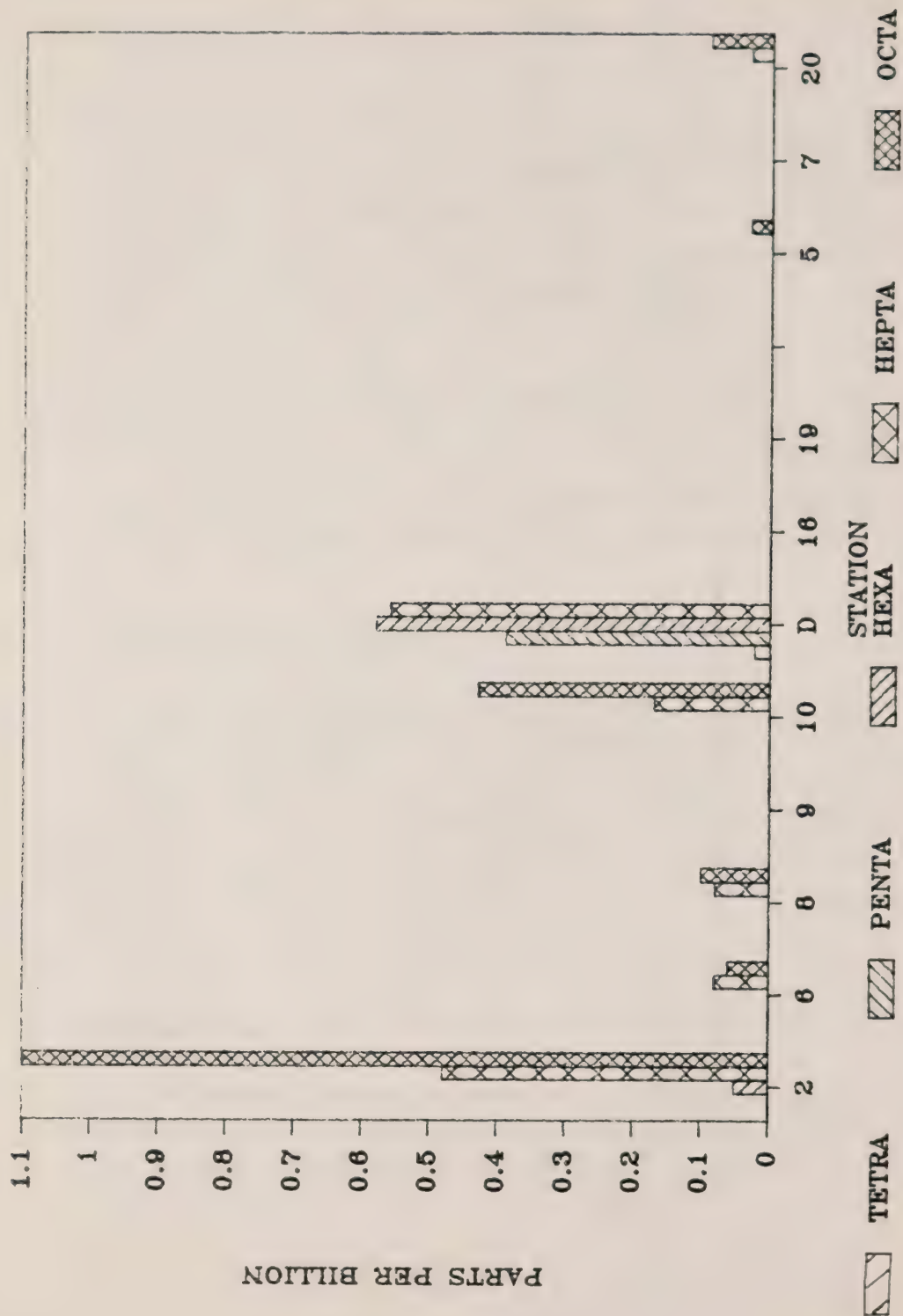


Figure 3.37 Chlorinated dioxin homologs in sediments from St. Clair River, 1985.

Mercury Contamination of St. Clair River Sediment

The concentration of total mercury was determined in individual sediment subsamples from cores No. 10X, 10Z, 13B, 16A, 17A, and 18A. A brief description of each core and the concentration of total mercury in the subsamples are given in Table 3.14.

The concentration of mercury was found to range from 0.070 to 2.565 $\mu\text{g/g}$ in Lake St. Clair surface sediments in 1970, representing about a threefold increase in the average concentration over that observed in Lake Huron. Thomas (1974) and Wolery and Walters (1974) indicated that the high mercury loading which occurred in the St. Clair/Detroit River system resulted from inputs from the Dow chloralkali plant in Sarnia, and possibly other industrial sources along these rivers until 1970. A significant decrease in mercury concentration was observed in Lake St. Clair sediments after 1970 (Thomas *et al.*, 1975; Mudroch, 1985, unpublished data). This observation indicates a decrease in mercury loadings to the St. Clair River which followed the revision and control of the discharge of mercury by Dow chloralkali plant at the beginning of the 1970s.

In this survey, sections which had more tarry material and a strong, oily odour contained a higher concentration of mercury than the others. The concentration of mercury at station 13B was much higher than at station 10X or 10Z. About ten times lower concentration was found in 0- to 18-cm sediment at station 16A than at station 13B. However, the mercury concentration between 18- to 24-cm sediment depth at station 16A was similar to that found in core 13B. High concentration of mercury at 18- to 24-cm depth at station 16A reflects most likely some past inputs. This more contaminated sediment has been covered with sediment

TABLE 3.14. Concentration of Total Mercury and Sediment Description

Sample	Mercury Concentration µg/g	Sediment Description
Core 10 X		
0 - 3 cm	0.45	About 6 cm long core of coarse sand and gravel with no odour.
3 - 6 cm	0.44	
Core 10 Z		
0 - 3 cm	0.18	0-9 cm of greyish brown, fine, well sorted sand with a 0.5 cm layer of fine silty clay on the top of the core. Some black spots with odour in this whole section. From 9-14 cm greyish brown fine to medium sand with some dark spots and light coloured fibres (up to 4 cm long, about 0.2 cm thick - look like plastic). From 14-20 cm greyish brown medium sand with 2 pieces of black material (about 3 cm dia.) and a fish bone (4 cm long, 0.4 cm thick). This section has a strong odour.
3 - 6 cm	0.19 dupl.	
	0.14	
Core 13 B		
0 - 3 cm	28.0	About 33 cm of greyish brown to dark grey medium to coarse sand with some black pebbles (<1 cm dia.) at the surface of the core. The 0-2 cm section appears to be clean with no odour. A distinct division exists at 2 cm depth from clean sand to greyish brown-dark grey sand with a strong odour. Sand grains appear to stick together. A light grey rubber-like agglomerate (about 6 cm dia.) with a strong, solvent-like odour was found at 6 cm depth. The whole core below 6 cm had a very strong odour. However, the odour seemed to be strongest at the 6-12 cm depth.
3 - 6 cm	43.0	
6 - 11 cm	36.0	
Core 16 A		
0 - 3 cm	3.3	About 24 cm of greyish brown to dark grey sand, finer at the 0-1 cm top of the core. Below 1 cm, the sediment consists of coarse sand and some pebbles. Below 6 cm some "larry" black material appears to increase in quantity towards the bottom of the core. The sediment below 3 cm has a strong odour increasing gradually towards the bottom of the core.
3 - 8 cm	3.4	
8 - 13 cm	4.3	
18 - 24 cm	35. dupl.	34.
Core 17 A		
0 - 3 cm	3.4	Fine sand
3 - 6 cm	9.7	
6 - 11 cm	4.8	
Core 18 A		
0 - 3 cm	3.8	Gravel and fine sand.
3 - 6 cm	9.9	
6 - 10 cm	1.3	

containing significantly lower concentrations of mercury. Radionuclide dating of this core indicated that the age ranged from 9 months for the top 3 cm to about 30 years for the deeper sections.

The concentration of mercury was similar in sections from cores 17A and 18A. The greatest concentration was found in the 3- to 6-cm section in both cores. However, the concentration of mercury decreased more rapidly in the 6- to 10-cm section in core 18A than 17A.

RECOMMENDATION

The presence of high concentrations of mercury in sediments opposite the Dow property should be investigated.

Sediments Trap Studies in Lake St. Clair 1985

Sediment traps which collect resuspended, recently deposited sediments moving in the water were installed in Lake St. Clair during the summer of 1985. Although a wide variety of organic contaminants were found in the samples (Oliver et al., 1986), only few compounds thought to originate from the Sarnia area - hexachlorobenzene, pentachlorobenzene, hexachlorobutadiene and octachlorostyrene - are reported in Figure 3.38.

In general, the concentrations of the contaminants are consistent with surficial sediment concentrations reported for 1984 and those published by University of Windsor (Oliver et al., 1986). The concentrations of HCBd are consistent with, although

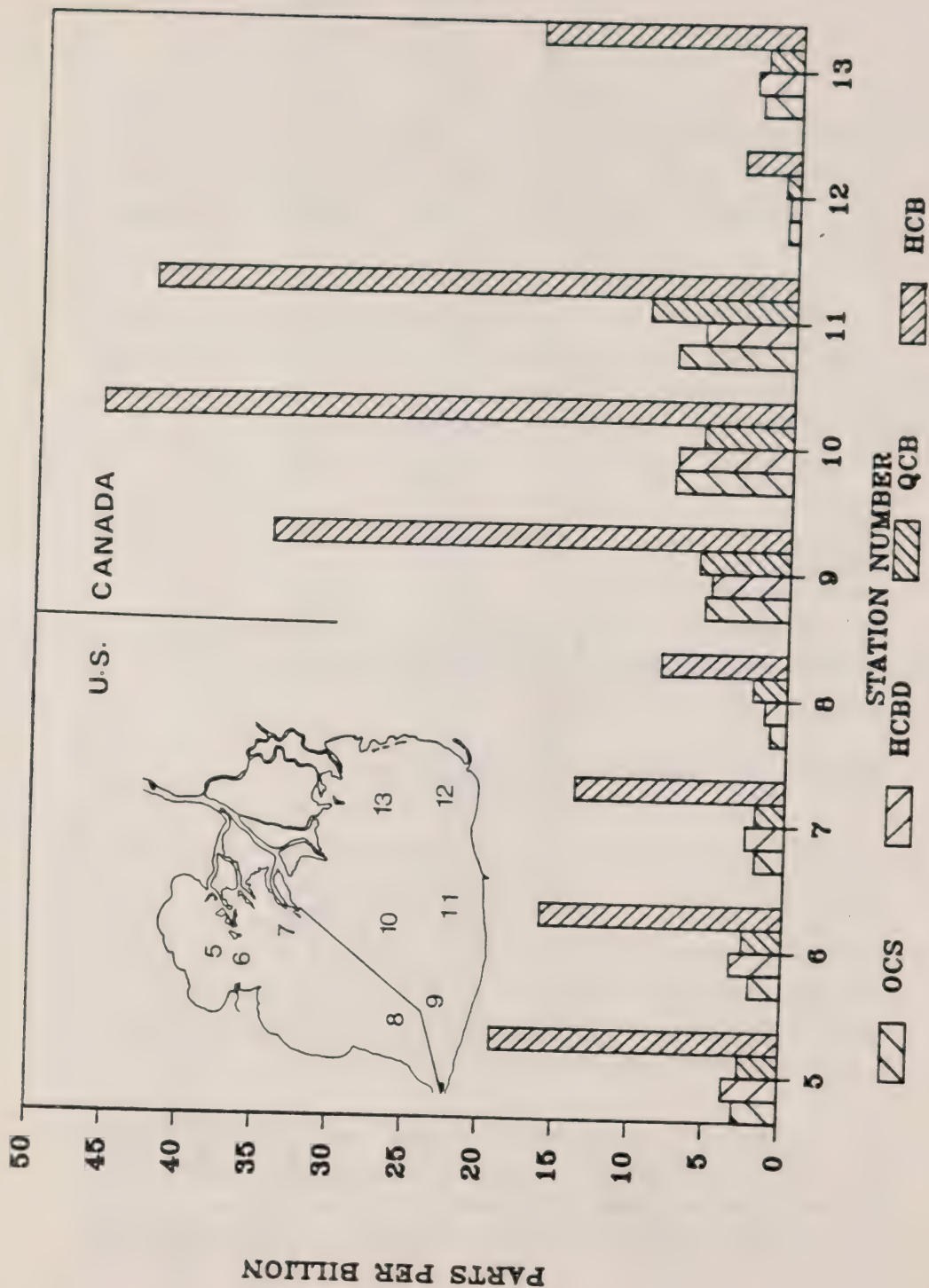


Figure 3.38 Sediment traps, Lake St. Clair suspended sediment, 1985.

lower than, those measured in the St. Clair River. The highest concentrations occurred at the stations (9, 10, 11) in the Canadian waters. Lower concentrations were found at stations (12, 13) near the eastern Canadian shore, and these may have been influenced by sediments derived from the Thames River.

Concentrations of the contaminants found in the traps in U.S. waters were about one-half those found typically in Canadian locations. The contaminants found at U.S. stations five and six (Anchor Bay) indicate that there is widespread dispersion. This may occur either through the U.S. side of the St. Clair River or by currents in the lake. Currents are generally thought to circulate and exit through the southern gap of Anchor Bay. This gives a higher probability that the contaminants are present in U.S. waters of the St. Clair River.

The ratios of one compound to another are similar between locations, which means that the compounds were probably introduced from a common source area.

Sediment Survey (MOE)

The Ontario Ministry of the Environment samples, which are described in this report, were collected during four phases:

- (1) During the summer of 1977, as part of the St. Clair River Organics Study, 50 surficial sediments (top 3 cm) located along the Ontario shoreline of the river were collected.

- (2) During the summer of 1983, surficial sediments were obtained from 25 stations located along transects across the river situated between Polysar and Dow/Suncor property line.
- (3) In the summer of 1985, surficial sediment grab samples were collected at 78 locations of which 29 stations were situated along the Michigan shoreline. This station grid extended from the river headwaters to the river delta.
- (4) In the fall (September) 1985, 24 surficial sediment samples were collected between the Township ditch and the southern property of Suncor. This survey was initiated in response to the Dow spill.

As part of the St. Clair Organics Study in 1977, sediments were analyzed for a number of organic and inorganic contaminants. At the time of the study, organic analyses were limited to PCBs and solvent extractable compounds. PCB levels ranged from 3 to 10 ppm and were mainly found along the Ontario shoreline of the river from the Township ditch to the southern end of the Suncor property. During the course of the 1977 study, oil globules were observed in the bottom sediments and were attributed to spills from industrial sources, freighters and docked ships during cargo handling. Solvent extractables, a measure of organic contamination, reached a maximum level of 28 000 ppm (2.8%) (MOE, 1979).

In view of the 1977 study, Dow Chemical initiated a sediment sampling program (1977 to 1984) which focused on the analyses of chlorinated organics. Although there was no interlaboratory

protocol established for comparison between Dow and MOE, Dow's results indicated levels similar to those obtained by MOE in 1983 and 1985. Recent survey data from Dow (1984, unpublished) revealed that the area in the vicinity of the 1st Street sewer complex was severely contaminated with hexachloroethane (HCE, 88 ppm), hexachlorobutadiene (HCBd, 400 ppm), pentachlorobenzene (OCB, 21 ppm), hexachlorobenzene (HCB, 600 ppm) and octachlorostyrene (OCS, 34 ppm).

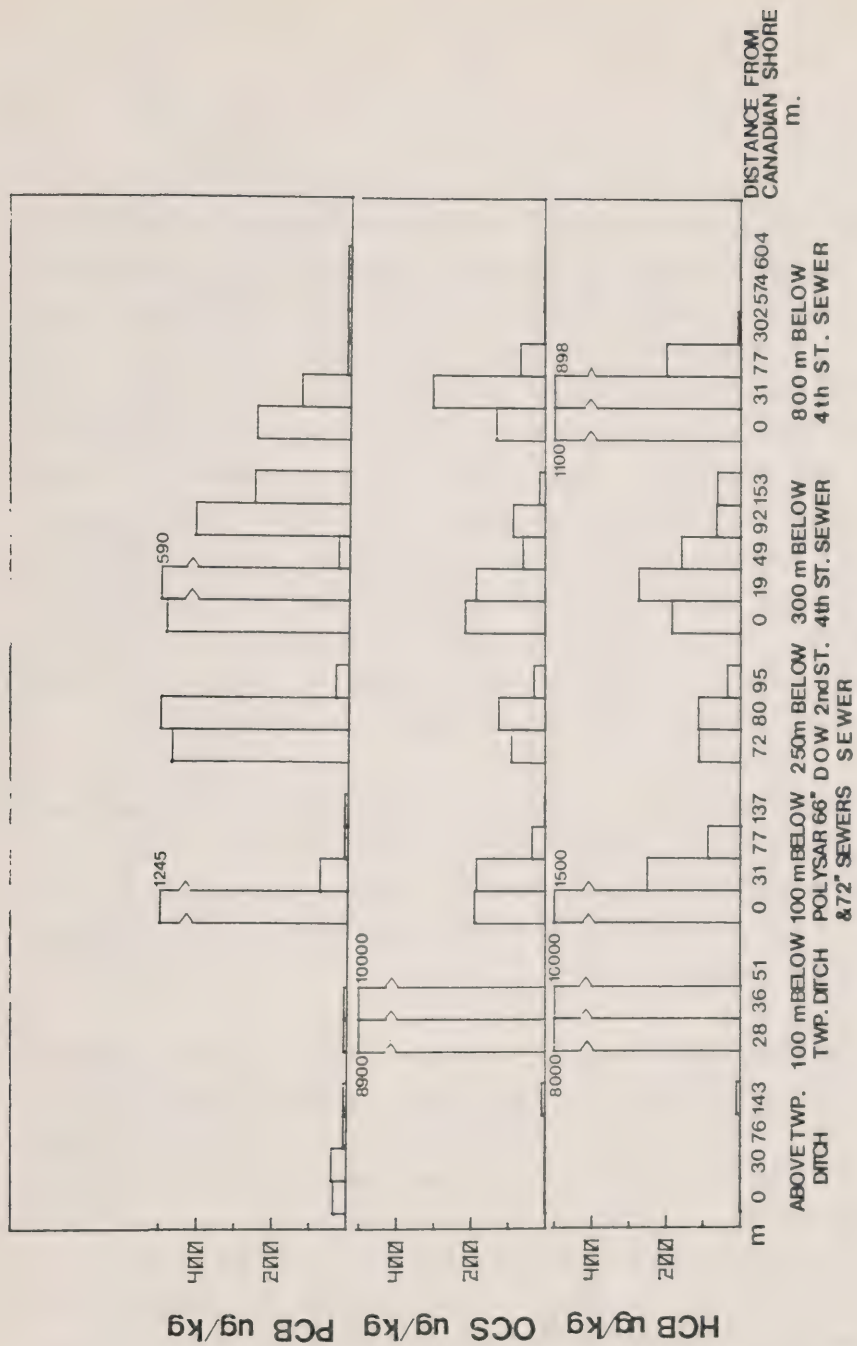
Investigations conducted by MOE in 1983 and 1985 (May and September) resulted in similar findings, while providing further delineation of the extent of sediment contamination.

The 1983 St. Clair River sediment survey focused on lateral and downstream distribution of PCBs, HCB, OCS and metals, lead and mercury. Transects were established at six locations from upstream of the Township ditch to opposite the Suncor intake. Findings are presented in Table 3.15 and Figure 3.39. Concentrations showed a declining trend with distance from the Canadian shore, both for organics and metals. There was no evidence for transboundary pollution as PCB, HCB and OCS concentrations were all below detection limits near the U.S. shoreline.

Major elevations in concentrations were noted downstream from the Township ditch. HCB and OCS increased 3 to 4 orders of magnitude from 1 to 10 $\mu\text{g/kg}$ above the Township ditch to 8 to 10 000 $\mu\text{g/kg}$ below. Continuous inputs along Polysar and Dow properties resulted in near shore levels in the ppm range for HCB. OCS and HCB declined rapidly downstream from the Township ditch and remained relatively constant at 1 ppm for HCB and 0.2 to 0.3 ppm for OCS. HCB and OCS levels persisted in sediments farther downstream as far as the Suncor shoreline.

Table 3.15 1983 St. Clair River Sediment Contaminant Levels

Distance from Canadian Shore (m)	PCB ($\mu\text{g/kg}$)	HCB ($\mu\text{g/kg}$)	OCS ($\mu\text{g/kg}$)	Pb ($\mu\text{g/kg}$)	Hg ($\mu\text{g/kg}$)
Upstream from the Township ditch					
143	20	12	10	12	0.01
76	20	1.0	1	128	0.04
30	40	2	1	19	0.02
0	35	1.0	1.0	15	0.02
Downstream from the Township ditch					
51	NA	1.0	NA	88	0.58
36	20	10 000	10 000	61	0.08
28	20	8 000	8 900	19	0.16
100 m Downstream from 66" and 72" sewers, opposite Tank Farm					
137	20	1	1.0	12	0.02
77	20	88	35	31	0.04
31	75	252	185	18	0.73
0	1245	1 500	190	22	100
250 m Downstream from 2nd Street sewer, opposite Dow's intakes					
95	35	35	30	10	15
80	500	114	125	11	29
72	470	112	90	8	21
300 m downstream from 4th Street sewer, opposite Dow/Suncor					
153	255	63	15	3.5	5.7
92	410	165	85	26.	1.0
49	30	160	60	17	2.3
19	590	275	185	12	3.8
0	485	185	215	29	14
Opposite Suncor intake					
604	20	1.0	1.0	9	0.02
574	20	1.0	1.0	5	0.01
302	20	9	1.0	3	0.01
77	20	200	65	11	0.67
31	130	1 100	300	78	7.9
0	250	898	139	15	3.5



STATION LOCATION

Figure 3.39 St. Clair River sediment contaminant levels, 1983.

Approximately 78 stations were sampled in both Canadian and American waters in May 1985. Figure 3.40 illustrates levels of PCBs, OCS and HCB found at locations extending from the CN tunnel to the southern extent of Suncor. No sediment contamination was observed in the immediate downstream vicinity of the tunnel. As in 1983, the Township ditch and 1st Street sewer complex are identified as major sources of PCB, OCS and HCB. A rapid decline along and across the river similar to that observed in 1983 occurred for all parameters; adjacent to the 1st Street sewer, however, values escalated into the ppm range. HCB remained in excess of 1 ppm (1247 $\mu\text{g/g}$), while PCB and OCS levels again dropped to below 0.5 ppm. Peak levels were measured 600 m below the 1st Street sewers for all three parameters, suggesting inputs from additional (i.e., 3rd Street sewer) Dow outfalls.

In response to a spill of perchloroethylene from Dow in August 1985, a further investigation to monitor impacts on sediments was undertaken. Sampling design was similar to the 1983 survey, as transects were positioned within a 2.5-km reach of the river adjacent to Dow.

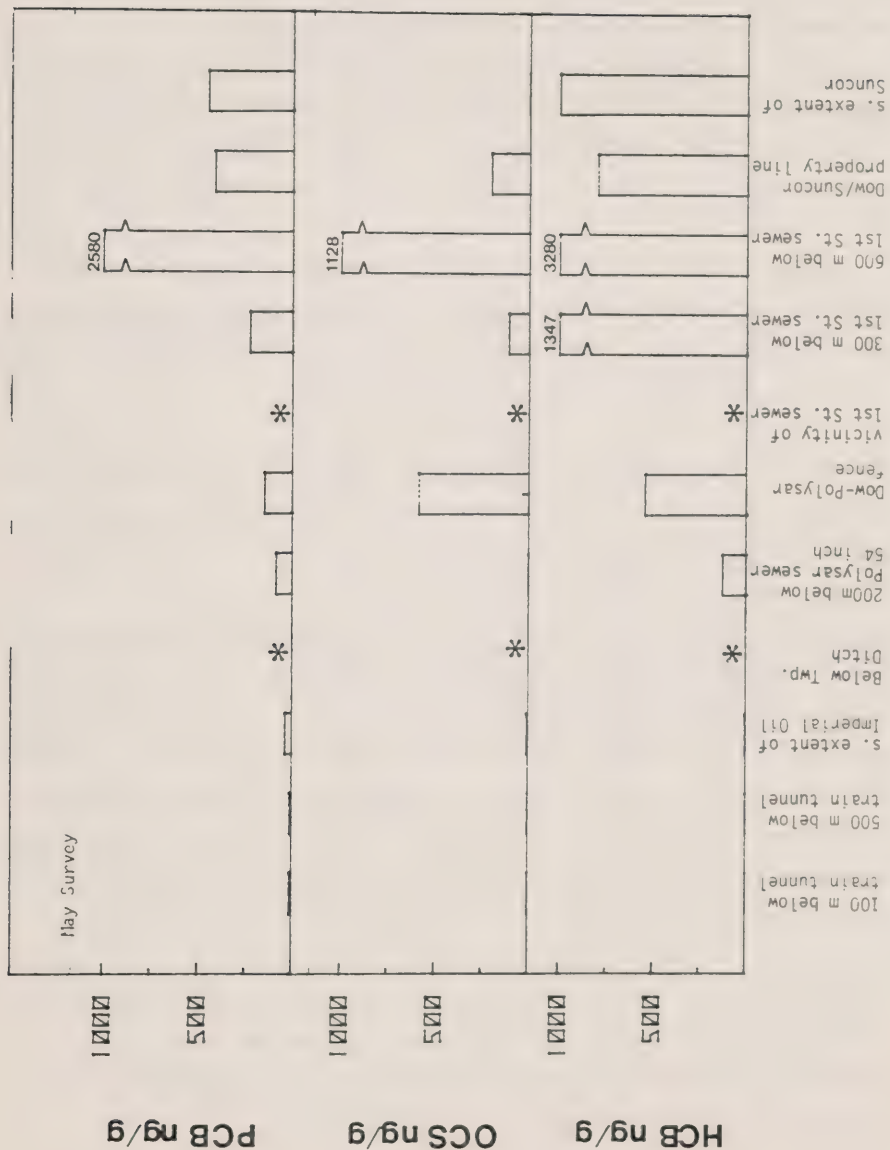
Chemical components of sediments from selected stations using full scan GC/MS (V. Taguchi, MOE, personal communication) are shown in Table 3.16. Compounds such as hexachloroethane, hexachlorobutadiene, perchloroethylene, hexachlorobenzene, pentachlorobutadiene, tetrachlorobenzene, pentachlorobenzene and octachlorostyrene were mainly confined to an area (40 x 300 m) in the vicinity of the 1st Street sewer. Most of the compounds were well below 0.1 ppm at or downstream from Suncor (1800 m downstream from 1st Street sewer complex) transect.

Table 3.16 Determination of Extractable Organic Compounds (ppm) in Sediments by GC/MS, September 1985

Compound	Upstream from Township Ditch 600 m Above 1st Street Sewers (40 m offshore)	Upstream from Dow's 1st Street Sewers (10 m offshore)	Opposite Dow's 1st Street Offshore Distance (10 m 40 m)	300 m Downstream from Dow's 1st Street Sewers (40 m offshore)	South end of Suncor 1800 m Below 1st Street Sewers (40 m offshore)	Walpole Island Water Treatment Plant	Wallaceburg Water Treatment Plant
Chlorinated Aliphatics:							
Carbon tetrachloride	0.1	0.1	0.2	+	0.1	+	+
Trichloroethylene	+	0.1	+	+	0.1	0.1	0.1
Pentachlorethane	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hexachloroethane	8	2	5	1	0.1	0.1	0.1
Tetrachlorethylene	29	10	10	2	1	+	+
Pentachloropropane	3	0.1	0.1	0.1	0.1	0.1	0.1
Pentachlorocyclopropane	0.3	0.1	0.1	0.1	0.1	0.1	0.1
Tetrachlorobutane	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hexachlorobutene	6	2	0.3	0.1	0.1	0.1	0.1
Pentachlorobutadiene	6 (2 isomers)	2 (2 isomers)	0.4 (2 isomers)	1	39	0.1	0.1
Hexachlorobutadiene	21	6	10	42	180	0.1	0.1
Tetrachlorobutadiene	0.3				9 (2 isomers)		
Octachlorocyclopentene	0.4						
Hexachlorotetrachlorobutane	3 (2 isomers)						

Table 3.16 Continued

Compound	Upstream from Township Ditch 600 m Above 1st Street Sewers (40 m offshore)	Upstream from Dow's 1st Street Sewers (10 m offshore)	Opposite Dow's 1st Street Offshore Distance (10 m 40 m)	300 m Downstream from Dow's 1st Street Sewers (40 m offshore)	South end of Suncor 1800 m Below 1st Street Sewers (40 m offshore)	Wallaceburg Water Treatment Plant
Chlorinated Aromatics:						
Heptachlorostyrene	3	12		13		
Octachloronaphthalene				0.9		
Dichlorobenzene				33	0.1	0.1
Tetrachlorobenzene	0.8	0.6	0.2	1	0.1	0.1
Pentachlorobenzene	0.9	6	0.9	6	0.1	0.1
Hexachlorobenzene	10	31	20	32	8	0.1
Octachlorostyrene	3	11	2	0.1	+	0.1
Polynuclear Aromatic Hydrocarbons:						
Sum of all measured values:	0.8	66	0.6	138.7	64	25.9
Miscellaneous:						
Biphenyl						
Diethyl Biphenyl			1	24	2	+
Alkyl Benzene		48.7	7	5	0.7	
Aliphatic Hydrocarbons	9 (11 isomers)		5 (9 isomers)	11	39	15
Terphenyl				130	20	20
Miscellaneous Phthalates			7	(19 isomers)	(20 isomers)	(28 isomers) (25 isomers)
Di-n-octylphthalate				47	7	27
Methyl Biphenyl				(6 isomers)	(11 isomers)	(11 isomers)
PCBs				15	8	
				1.3		



STATION LOCATION

Figure 3.40 St. Clair River near shore sediment contaminant levels, 1985. * unable to quantify due to interference

Surficial sediments (0 to 3 cm) were also analyzed for PCB/pesticides, volatiles and chlorinated aromatic hydrocarbons. Volatiles were determined by a headspace GC screening method as outlined in MOE's Handbook of Analytical Methods (1983). The identities of these volatile compounds should be considered tentative unless confirmed by mass spectrometry. The concentrations are to be considered minimum levels. However, the actual level in the sediments may not be higher than a factor of 2.

Hexachloroethane; 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene, 2,4,5-trichlorotoluene, hexachlorobenzene and octachlorostyrene were identified by routine GC analysis and generally confirmed results achieved by GC/MS.

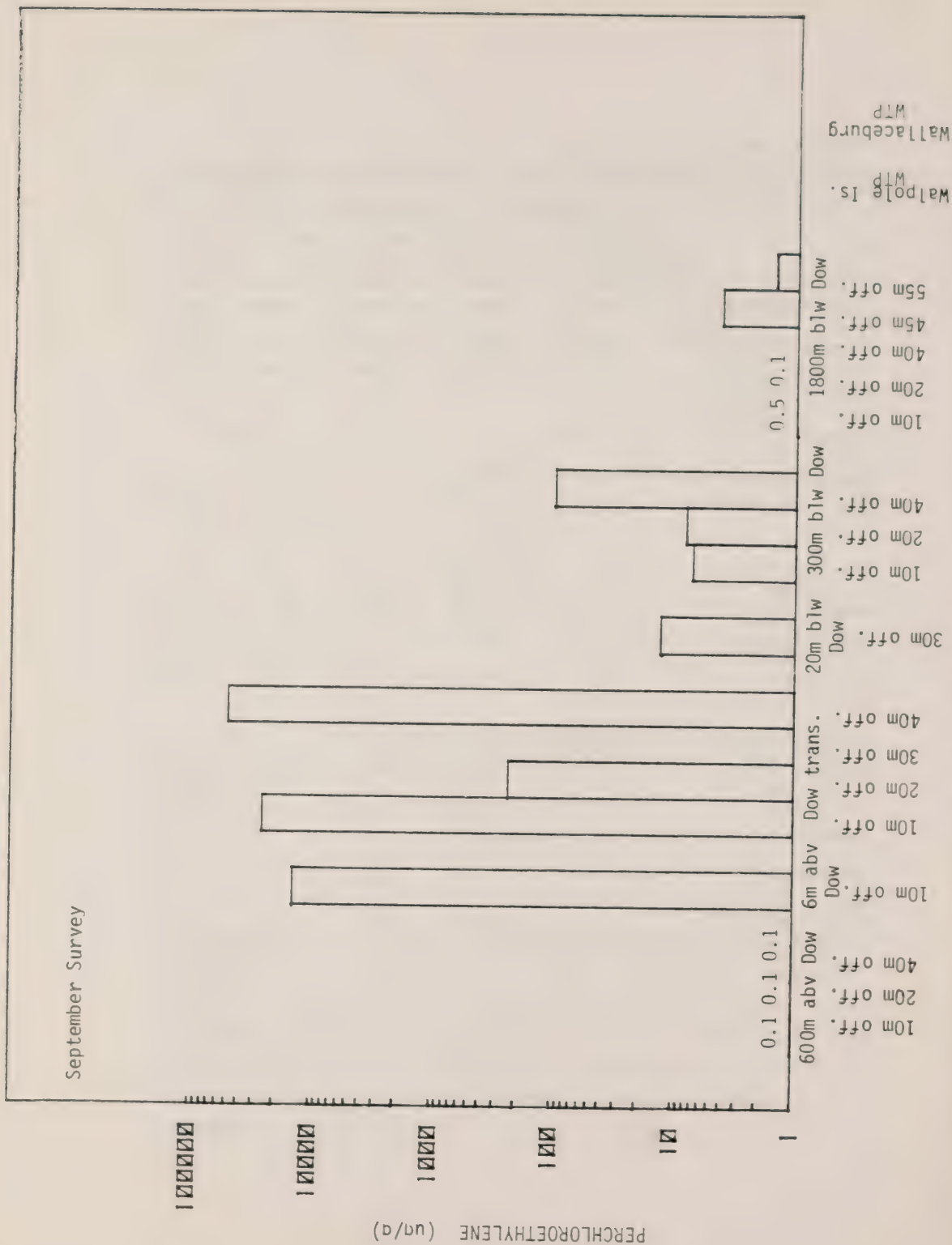
With the exception of hexachlorobenzene and octachlorostyrene, analyses for chlorinated aromatics are semi-quantitative and present a minimum value only.

Table 3.17 shows levels of perchloroethylene, hexachlorobenzene, octachlorostyrene and PCBs at selected locations along the Ontario shoreline of the river. Figures 3.41 to 3.45 illustrate profiles of contaminants at the above locations. Levels upstream from the Township ditch were representative of less significant inputs such as Imperial Oil, Sarnia Sewage Treatment Plant and non-point sources. Levels of perchloroethylene at this station ranged from 0.07 to 0.18 $\mu\text{g/g}$, HCB from 0.01 to 0.09 $\mu\text{g/g}$, OCS from 0.02 to 0.15 $\mu\text{g/g}$ and PCB from 0.02 to 0.15 $\mu\text{g/g}$. Increased levels were noted at a location just above Dow's 1st Street sewers. However, the HCB/OCS contaminant ratio of 2 was approximated to the upstream location value, indicating similar contaminant sources.

Table 3.17 Trace Organic Levels in Sediments, September 1985

Location	Analysis by Gas Chromatograph ($\mu\text{g/g}$)				
	Distance from Shore (m)	Compounds			
		Perc	HCB	OCS	PCB
Upstream from Township ditch	10	0.08	0.05	0.15	0.2
(600 m upstream from 1st Street sewers)	20	0.07	0.09	0.04	15
	40	0.18	0.01	0.02	0.05
Upstream from Dow's 1st Street sewers	10	14 000	64	35	2
Opposite Dow's 1st Street sewers	10	25 000	NA	NA	NA
	20	235	5.5	0.8	0.2
	40	49 000	133	26.0	2.0
300 m downstream from Dow's 1st Street sewers	10	7	2	0.03	0.13
	20	8	75	0.83	1.5
	40	100	1 000	5.3	76
Southern end of Suncor (1800 m downstream from 1st Street sewers)	10	0.1	0.73	0.15	0.08
	20	0.5	3.0	0.64	0.41
	40	NA	1.5	0.36	0.32
	45	4.2	0.8	0.30	0.42
	50	1.4	NA	NA	NA
Walpole WTP		0.05	0.06	0.03	0.2
Wallaceburg WTP		0.15	0.07	0.01	0.02

STATION LOCATION



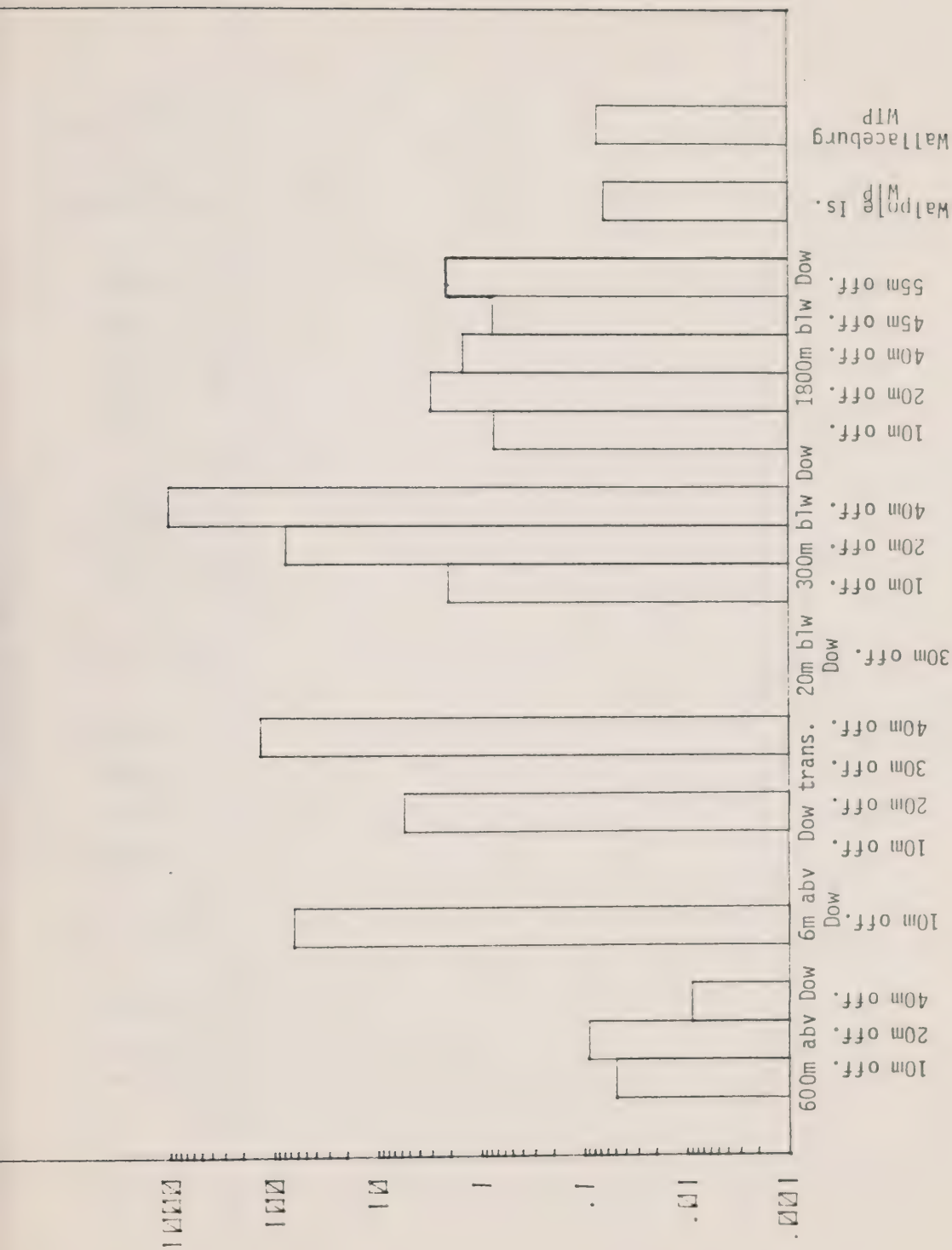
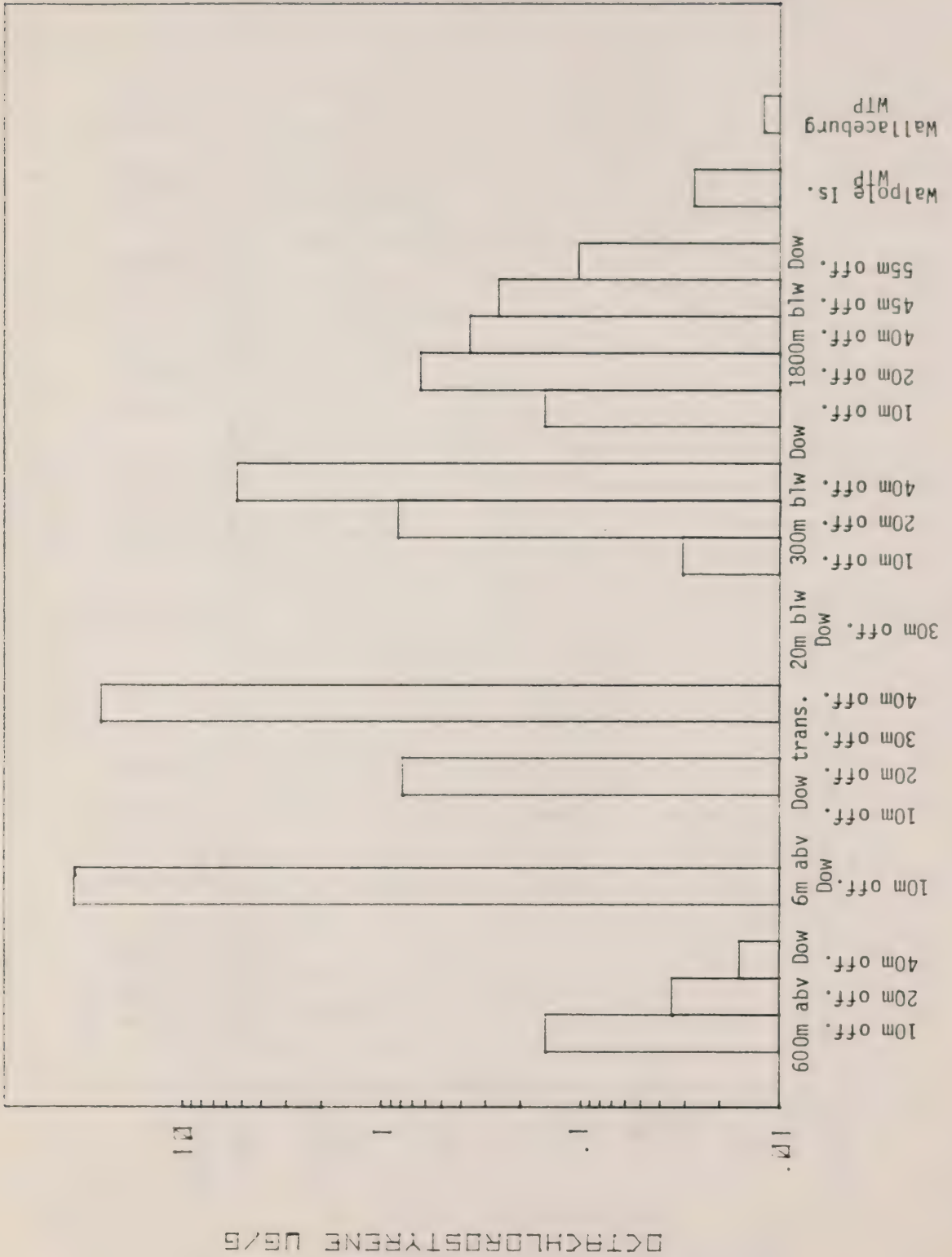
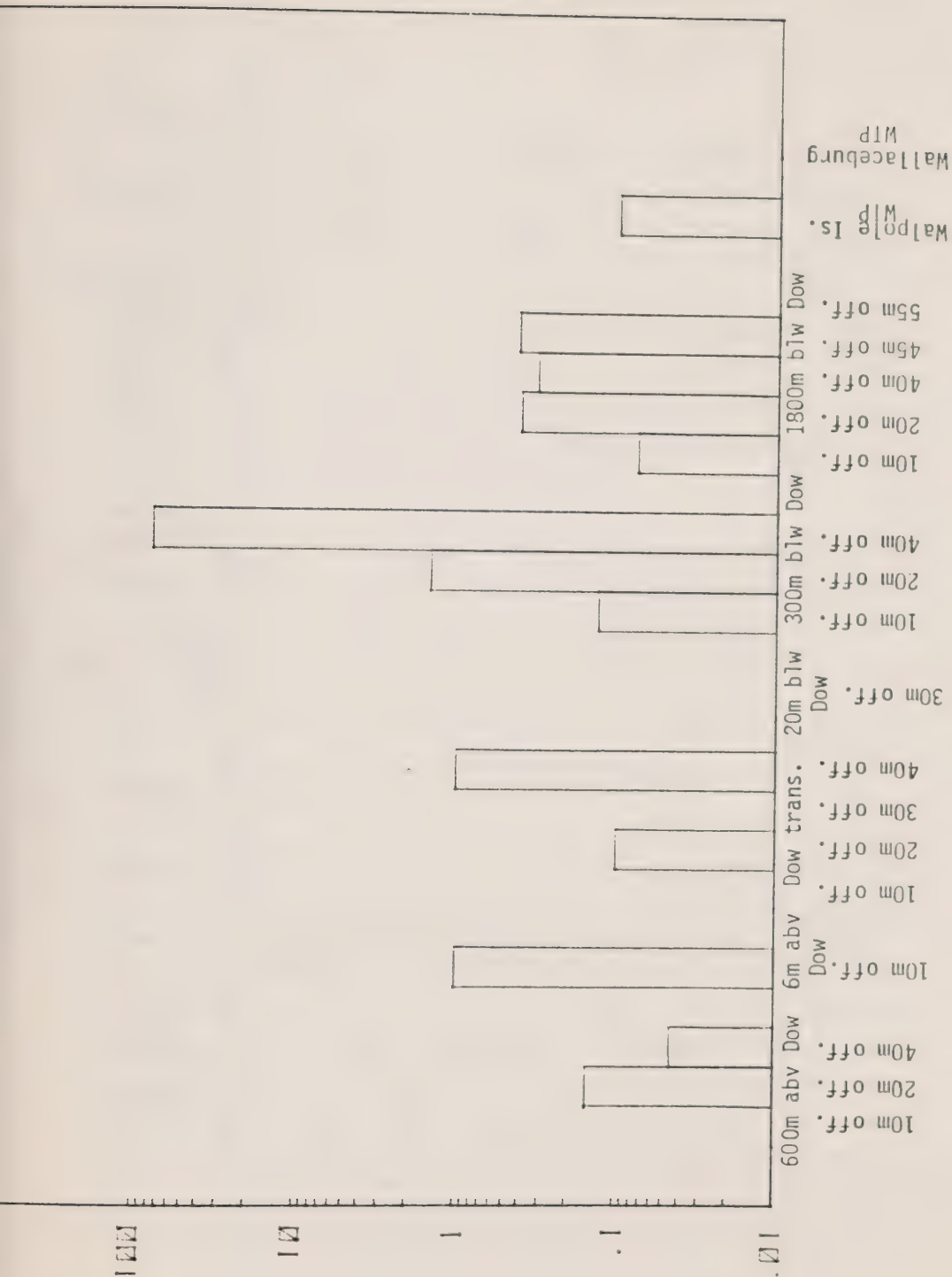


Figure 3.42 St. Clair River sediment contaminant levels, 1985.



STATION LOCATION

Figure 3.43 St. Clair River sediment contaminant levels, 1985

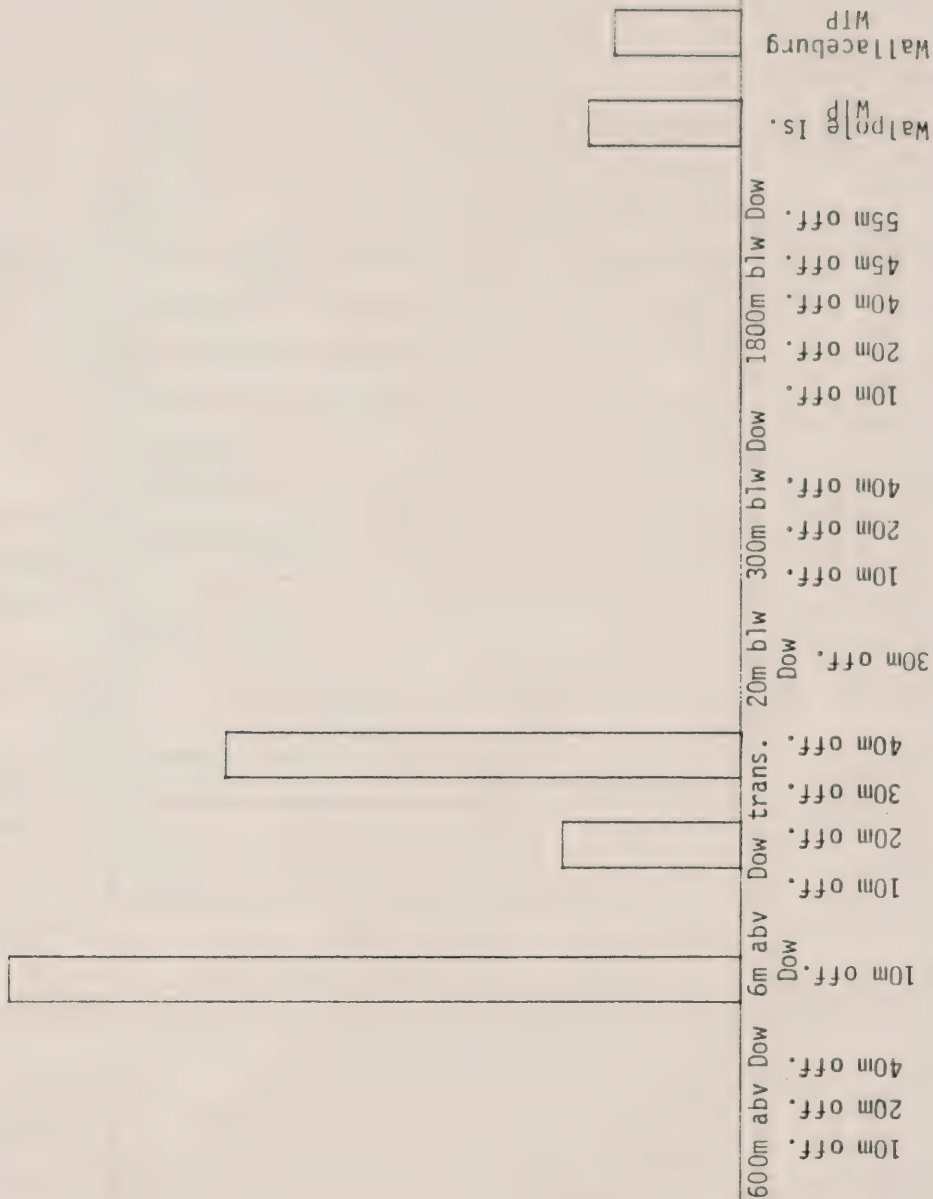


STATION LOCATION

Figure 3.44 St. Clair River sediment contaminant levels, 1985.

HEXACHLOROCYCLOPENTADIENE UG/G

0.01
0.1
1
10
100



STATION LOCATION
Figure 3-45 St. Clair River sediment contaminant levels, 1985.

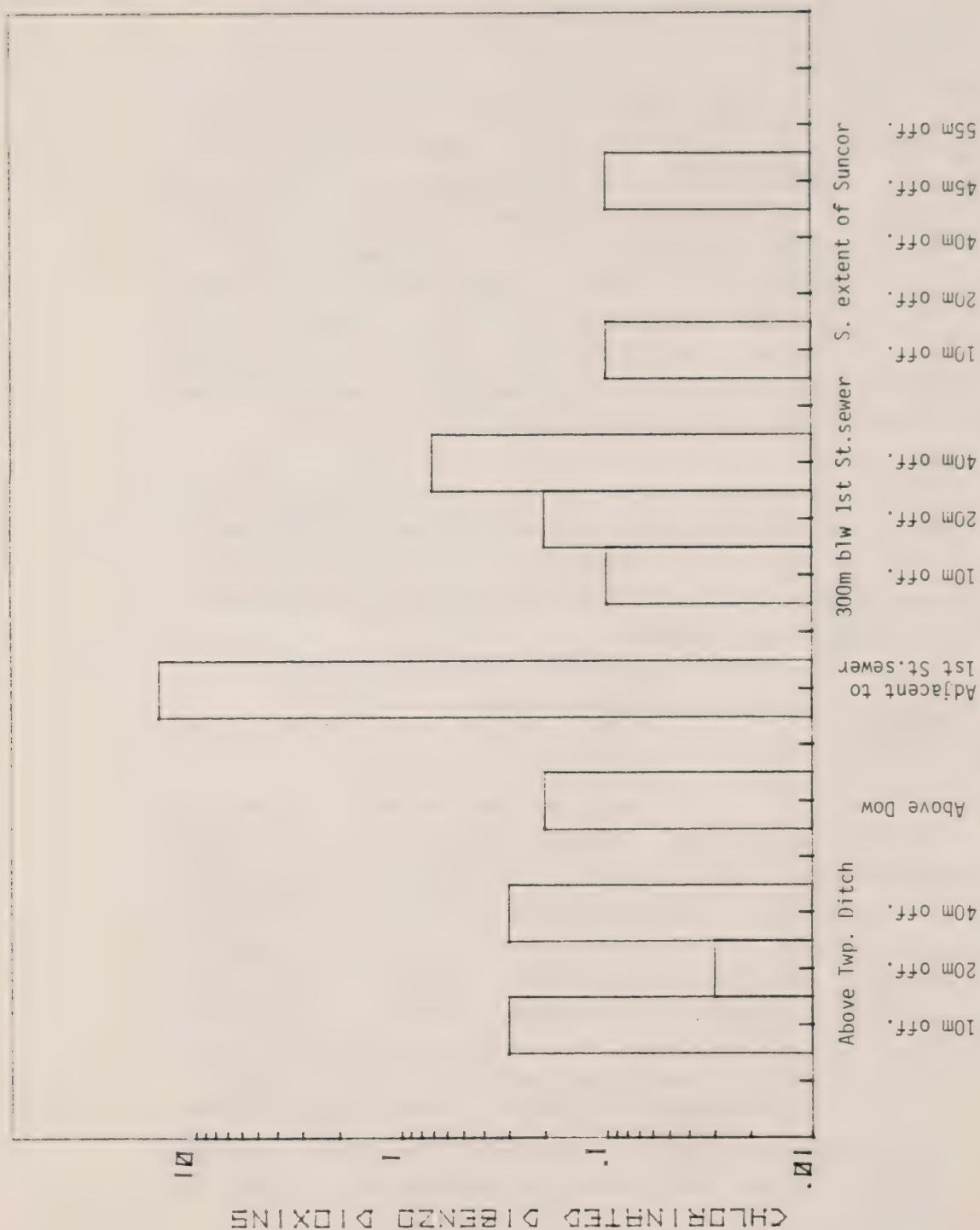
Perchloroethylene values increased to 14 000 ppm, indicating the effect of the spill. In an area opposite Dow's 1st Street sewer complex, levels of perchloroethylene were 49 000 µg/g (4.9%) at 40 m offshore. Extremely high perchloroethylene concentrations in this area are the result of small globules of tarry material in the sediment. Farther downstream from Dow's 1st Street sewers, perchloroethylene levels decreased to 100 µg/g at 40 m offshore. The HCB/OCS ratio increased to between 5 and 200, indicating inputs of these chemicals are mainly from Dow sources rather than the Township ditch.

The patterns of higher levels offshore as compared with those near shore were also observed in the monitoring of bottom waters in the 1st Street sewers area. The effect of these high levels is localized, since significant decreases were observed at the southern end of Suncor.

Dioxins

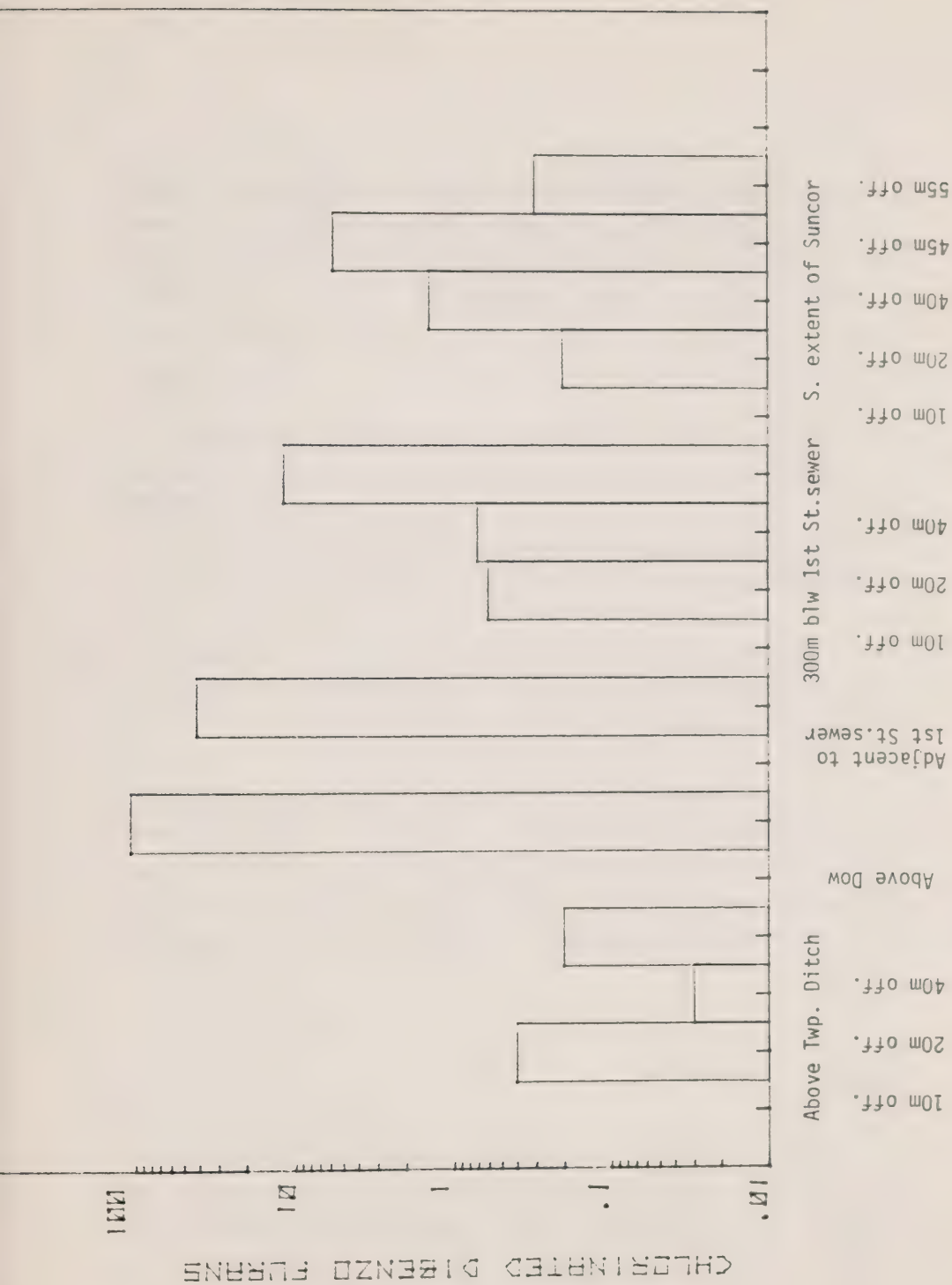
Profiles of dioxins along the shore are shown in Figures 3.46 and 3.47. Sediments upstream from the Township ditch (southern end of Imperial Oil) contained total chlorinated dibenzo-p-dioxins of 0.2 ppb at 10 m offshore, 0.03 ppb at 20 m offshore, and 0.3 ppb at 40 m offshore. The only congeners detected were octachloro-dioxins. Similarly, the total chlorinated dibenzofurans consisted primarily of octachloro-furans at 0.3 ppb levels 10 m offshore and 0.03 ppb 20 m offshore. No chlorinated furans were detected at 40 m offshore.

Concentrations of total chlorinated dibenzofurans increased to 106 ppb just above Dow's 1st Street sewers. Octa- and



ST. CLAIR RIVER STN.

Figure 3.46 Total dibenzo-dioxins (ng/g).



CLAIR RIVER STN.

Figure 3.47 Total dibenzo-furans (ng/g).

heptachloro-furans were the main congeners at levels of 95 and 7.5 ppb, respectively. A level of 0.2 ppb tetrachloro-dioxins (2 isomers) was the only dioxin congener found. Total chlorinated dibenzodioxins increased to 15.2 ppb in sediments located opposite the 1st Street sewers, whereas total dibenzofurans decreased to 40.6 ppb.

Levels of total chlorinated dibenzofurans downstream from the 1st Street sewers amounted to 11.5 ppb at 40 m offshore. Locations near the shore (at 10 and 20 m offshore) exhibited 0.6 ppb total chlorinated dibenzofurans, the main congeners being hepta- and octa-.

A maximum total dibenzodioxin level of 0.7 ppb (primarily octachloro-dioxin) was detected at the 40 m offshore site coinciding with the maxima observed for dibenzofurans.

Farther downstream, at the southern end of Suncor, levels of total chlorinated dibenzodioxins decreased to 0.1 ppb and total chlorinated dibenzofurans decreased to 5.6 ppb. At Walpole and Wallaceburg water intakes, both chlorinated dibenzodioxins and chlorinated dibenzofurans were generally at or below detection levels.

Summary

Both MOE and DOE surveys found two hot spots for HCB, QCB, HCB and OCS, which are major by-products of the production of chlorine and chlorinated solvents. These stations were near the Township ditch, which drains the Dow Scott Road landfill site, and in the vicinity of the Dow 1st Street sewer complex. The

most significant of these two sources appears to be Dow's 1st Street sewers. This contamination is a consequence of perchloroethylene liquid losses in conjunction with continuous discharges of the above chlorinated organics.

RECOMMENDATION

Losses of liquid perchloroethylene, carbon tetrachloride should be curtailed. Causes of these losses should be determined.

Evaluation to ascertain the effect of contaminated sediments on the biota and water column should be undertaken.

BIOLOGICAL SURVEYS

Community Structure Analysis

The health of the macrozoobenthic community of the St. Clair River was assessed in 1968, 1977 and twice in 1985 (May and November). The November 1985 survey was designed to assess the impact of an August spill of perchloroethylene from Dow and delineate the extent of impact. In each survey, samples were taken by Ponar grab and processed as described in Thornley (1985) and Griffiths (1985).

Indicators of pollution (tubificids 80% of total number of benthic organisms and for environmentally sensitive organisms (*Hexagenia limbata*)) were used to provide insight into the health of the benthic fauna as related to impacts of industrial and municipal discharges.

Along the Ontario shoreline of the St. Clair River upstream from major point sources as well as on the Michigan side of the river where there is little municipal or industrial development, the benthic communities were balanced in terms of pollution tolerant, intolerant and facultative organisms in both the 1968 and 1977 surveys. A greater number of organisms per square metre and a greater number of taxa were found in the 1977 survey.

In the 1968 survey (MOE, 1979), the benthic community was impaired on the Ontario side of the river, downstream from the petrochemical complex. From this point down to the mouth of the river, no pollution sensitive organisms were found, the number of taxa per station was 5 to 7 compared with 9 to 13 at the upstream

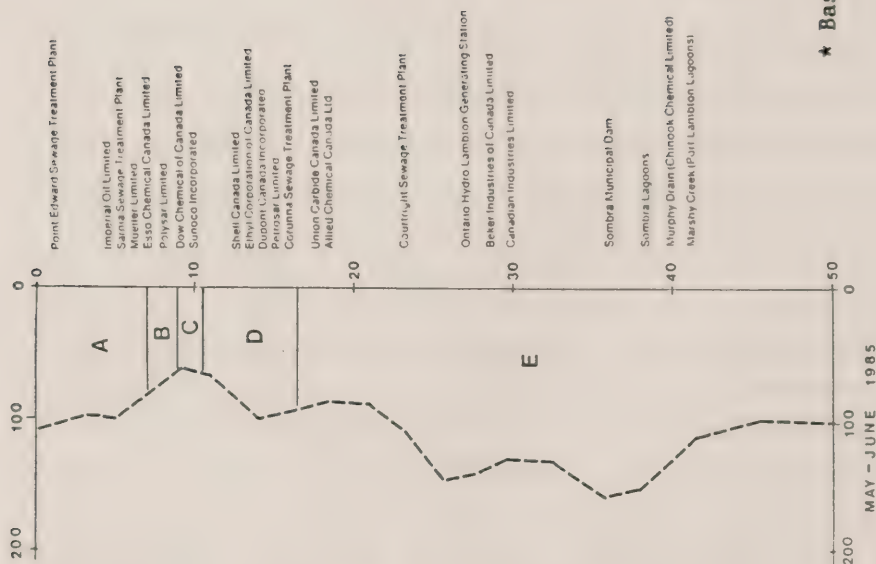
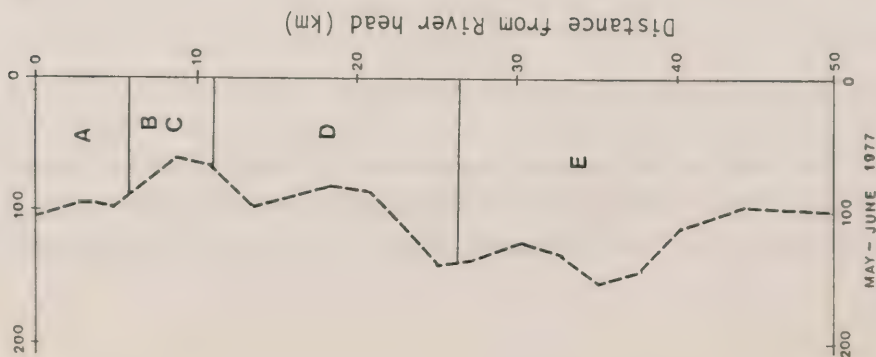
and Michigan sites, and pollution-tolerant forms dominated the community.

Results of the 1977 survey (MOE, 1979) indicated significantly improved, but still impaired, conditions. The numbers of taxa per station in the lower river had increased compared with the 1968 results, some pollution sensitive organisms had reappeared in the lower river. However, the distribution of Hexagenia did not change over the 1968 to 1977 period. Hexagenia were found at 16% of stations sampled in 1968 and at 15% in 1977.

The May 1985 survey (MOE, 1986) revealed changes in the benthic community which suggest that water quality conditions of the whole river have improved. A comparison of water quality zones between 1977 and 1985 indicate that the down river zone of good water quality advanced up river approximately 10 km over the eight years. In addition, water quality conditions within the impacted and recovery zone have improved since 1977 (Fig. 3.48). Low densities of some pollution intolerant benthic species which were absent from the impacted zone in 1977 were present at most stations in the impacted zone in 1985. A general increase in species richness was also observed in the recovery zone over 1977.

In November 1985, a benthic survey was carried out in response to the Dow spill between the Township ditch and the southern end of Suncor. A comparison of the results of the May and November 1985 surveys for the above area showed that there was generally an increase in the number of taxa per station in November but little change in abundance of organisms per square metre. This is an effect of seasonality. However, in an area extending about 100 m downstream from Dow's 1st Street sewer

Distance from shore
(m)



LEGEND

- A -- good water quality
- B -- Impacted water quality
- C -- seriously impacted water quality
- D -- recovery zone
- E -- good water quality

★ Based on Health of Macrozoobenthic communities.

Figure 3.48 Water quality zones of the St. Clair River in May-June of 1977 and 1985.

complex there were changes in the benthic community inconsistent with the changes attributed to seasonality. In this zone, a reduction in the number of taxa, a reduced abundance and an absence of certain species of invertebrates indicated that the invertebrate fauna had been negatively affected by impaired water quality conditions. The perchloroethylene spill which entered the river via Dow's 1st Street sewer was probably responsible for the impairment of water quality.

The benthic community of Lake St. Clair was assessed in 1977 (Hiltunen and Manny, 1982) and in 1983 (MOE, unpublished). Nowhere in Lake St. Clair in 1983 did the percentage of tubificids exceed 60%, indicating good water quality conditions in the lake. The sensitive mayfly Hexagenia limbata was well represented in both 1977 and 1983, and distribution seemed to be influenced more by substrate than by water quality.

In summary, although sections of the St. Clair River still show an impaired benthic community, especially in the immediate area of the petrochemical industry, conditions have improved markedly since the initial 1968 surveys. The August 1985 spill of perchloroethylene from Dow Chemical Co. was the probable cause of a degraded benthic community in a 100 m stretch of river downstream from Dow's 1st Street sewer complex.

ACUTE LETHALITY OF SEDIMENTS

Laboratory bioassays were conducted on the sediment from the St. Clair River in the vicinity of the spill. The objective of the bioassays was to determine whether the sediments in the

vicinity of the spill could be toxic to benthic or other organisms in the area.

The major concern in carrying out these studies, was that the methods used are presently in the developmental stage. No standardized protocol exists for either carrying out sediment bioassays or for interpreting the results. Notwithstanding the above, the results of this study provide some insight into the impact of the spill on biota.

The organisms selected for the sediment bioassay are indigenous to the St. Clair River. The test organisms include a benthic invertebrate Hexagenia limbata, which is a burrowing mayfly, an epibenthic organism Hyallela azteca, which is an amphipod that lives at the sediment water interface, and the fathead minnow (Pimphales promelas).

Invertebrate and vertebrate organisms were exposed in separate 1.5-L containers for a period of 96 ± 4 hours. Dissolved oxygen levels were maintained at or near saturation, while temperatures remained at ambient levels and varied between 19° and 23°C. At the end of each test, mortality was assessed based on the presence or absence of movement.

Tests were carried out on two sets of sediments. The first set was collected September 23 to 28, 1985, from Sarnia Bay; between Polysar and Dow; and immediately below the Dow 1st Street sewer discharge. Sediments were collected by Ponar grab and shipped unrefrigerated to the MOE laboratory in Toronto. Upon receipt, sediments were refrigerated at 4°C until tests were begun. A screening bioassay was conducted on the sediments to give preliminary indications of toxicity (Table 3.18a).

Table 3.18a Preliminary Bioassay Results on Sediments Collected in the St. Clair River September 23-28, 1985

Station	Percent Survival		
	Fathead Minnows	<u>H. azteca</u>	<u>H. limbata</u>
<u>Sarnia Bay</u>			
Control	100	90	100
Below Polysar above Dow	80	0	100
Below Dow	0	0	50

Table 3.18b Bioassay Results on Sediments Collected in the St. Clair River November 3-7, 1985

Station	Rep #	Percent Survival		
		Fathead Minnows	<u>H. azteca</u>	<u>H. limbata</u>
<u>Sarnia Bay</u>				
Control	1	100	90	100
	1	100	90	100
Below Polysar above Dow	1	80	0	80
	2	100	0	80
Below Dow	1	100	0	100
	2	100	0	80
200 m below 1st Street outfall	1	100	0	100
	2	100	0	80
400 m below 1st Street outfall	1	80	90	80
	2	100	40	80

Table 3.18c Bioassay Results of Comparison Between Sediments Collected in the St. Clair River September 23-28 and November 3-7, 1985

Station	Rep #	Percent Survival		
		Fathead Minnows	<u>H. azteca</u>	<u>H. limbata</u>
<u>Sarnia Bay</u>				
Control	S*	100	100	80
	N*	100	90	80
Below Polysar above Dow	S	100	0	60
	N	100	0	100
Below Dow	S	0	0	0
	N	100	0	100
200 m below 1st Street outfall	N	100	0	100
400 m below 1st Street outfall	N	100	0	80
Spike 2%	Rep 1	100	80	80
Spike 2%	Rep 2	100	60	80

* S - September 23-28, 1985; N - November 3-7, 1985.

A second set of sediments was collected (November 3 to 7) from the same three locations as in the original collection and additionally at 200 and 400 m below the 1st Street outfalls to determine the spatial extent of the zone of impact. Results of bioassays on these sediments, run in duplicate, are presented in Table 3.18b.

A further comparison was made between samples collected at all locations for both sediment sets (Table 3.18c). To determine if perchloroethylene was responsible for the mortality observed in this bioassay, control sediments from Sarnia Bay were spiked with reagent grade "Baker Analyzed" perchloroethylene.

Results and Discussion

The results of the sediment bioassay indicate that sediments in the St. Clair River above the "chemical valley" are not acutely toxic (defined as 100% mortality). However, within the chemical valley this situation changes. The sediments collected upstream from Dow's discharge but within the chemical valley are acutely toxic to some species of benthic invertebrates. The sediments directly upstream from Dow were to serve as a control and it was expected that there would be little or no mortality of the test organisms. However, the sediments are toxic to H. azteca and some mortality occurred in both the fathead minnows and H. limbata. This finding complicates any interpretation that is to be made of the effects of the Dow spill of perchloroethylene.

In the bioassays conducted on the Dow sediments collected in September, the results of both the preliminary and subsequent

experiments were similar and indicated that the sediments were acutely toxic to organisms living in, on or above the sediments. However, the bioassays on spiked sediments suggest that the toxicity of the Dow sediments was not due solely to the perchloroethylene. Further data on the perchloroethylene levels as well as other compounds in the sediments are required to confirm this.

By the time the sediments had been collected in November, the situation had changed. The toxicity of the sediments had declined considerably. Although the sediments elicited an immediate behavioural response in fathead minnows, within hours, this response disappeared and the fish behaved similarly to those of the control. Since the results of Polysar station sediments and Dow station sediments are essentially the same, it is concluded that there was no longer a toxic effect from the perchloroethylene or, that the test methods were not sensitive enough to detect it.

In summary, the methods used in this study, while still in the developmental stage, show promise for assessing the toxicity of sediments. The test results appear to be reproducible and logical. Relatively uncontaminated sediments, in this case the Sarnia Bay sediments, produce very little mortality, whereas, the sediments which are most contaminated, resulted in almost total mortality.

Contaminants in Biota

Information has been obtained by the Ministry of the Environment concerning the bioaccumulation of contaminants by aquatic organisms and distribution in the environment along the St. Clair River system (Appendix). These include the uptake of contaminants by the attached alga Cladophera, by clean clams (Elliptio complanatus) introduced in cages to the river environment, by young fish collected to reflect the significance of localized sources and by sport fish species collected under the Ministry's Sport Fish Contaminant Monitoring Program. Results for these various programs reinforce the information provided in the earlier sections of this report concerning principal areas affected by contaminants and demonstrate the potential impacts on aquatic life and the fishery potential of the waterway through the bio-uptake mechanisms substantiated.

Contaminants in Young Fish

Collections of indigenous juvenile spottail shiners (Notropis hudsonius), emerald shiners (Notropis atherinoides) and yellow perch were taken in various years at three sites in the St. Clair River, four sites in Lake St. Clair, and at a control site in Lake Huron (Fig. 3.49). Fish on one or more occasions have been analyzed for PCBs, DDT, mirex, BHC, chlordane, HCB, OCS, PAHs, perchloroethylene, polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF), Hg and Pb. Collection methods are described in Suns et al. (1985) and analytical protocols in Ontario Ministry of the Environment (1981). Results are based on whole fish composites, each composite being a collection of 10 fish. Data were examined for spatial distribution in the

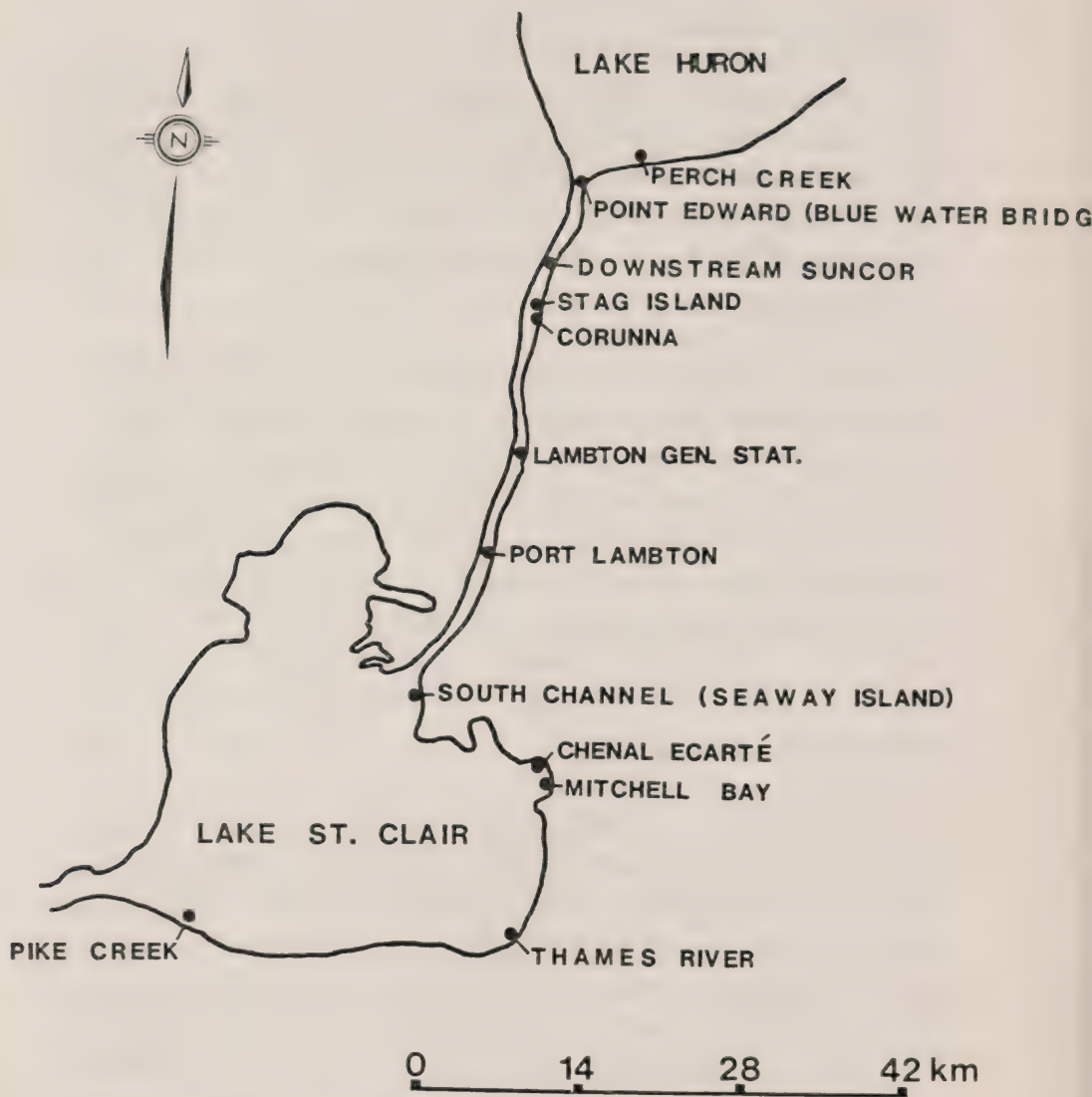


Figure 3.49 Spottail shiner sampling locations.

St. Clair River/Lake St. Clair to identify areas of concern for point source identification. Some data were also evaluated for temporal trends as collections at one station (Pike Creek) in Lake St. Clair began in 1978.

PCBs, DDT, Mirex, BHC, Chlordane

With the exception of the Suncor collection from the St. Clair River, PCB residues in the other St. Clair River and Lake St. Clair young-of-the-year spottail shiner collections were below the IJC Aquatic Life Guideline (100 ng/g). PCBs in spottail shiners at Suncor were significantly ($P < 0.01$) elevated when compared to the Lake Huron control at Perch Creek (Fig. 3.50). PCB residues in spottail shiners from Lake St. Clair at Pike Creek have declined significantly ($P < 0.01$) since 1978 (Fig. 3.51). However, PCB residue reductions during the 1980's have slowed considerably.

Total DDT residues in all young-of-the-year spottail shiners from the St. Clair River and Lake St. Clair were below the IJC Aquatic Life Guideline of 500 ng/g. While there have been total DDT residue changes in spottail shiners from Pike Creek, there is no evidence of developing trends at this time. Mirex residues were not detected in any St. Clair River and Lake St. Clair spottail shiners

Total BHC and total chlordane residues were generally lower in the St. Clair River and Lake St. Clair collections than residues in spottail shiners from Lake Huron at Perch Creek. Chlordane residues in spottail shiners from Lake St. Clair at

Organochlorine residues in 1982/83 young-of-the-year spottail shiner collections from Lake Huron, the St. Clair River and Lake St. Clair (means \pm 95% C.L.).

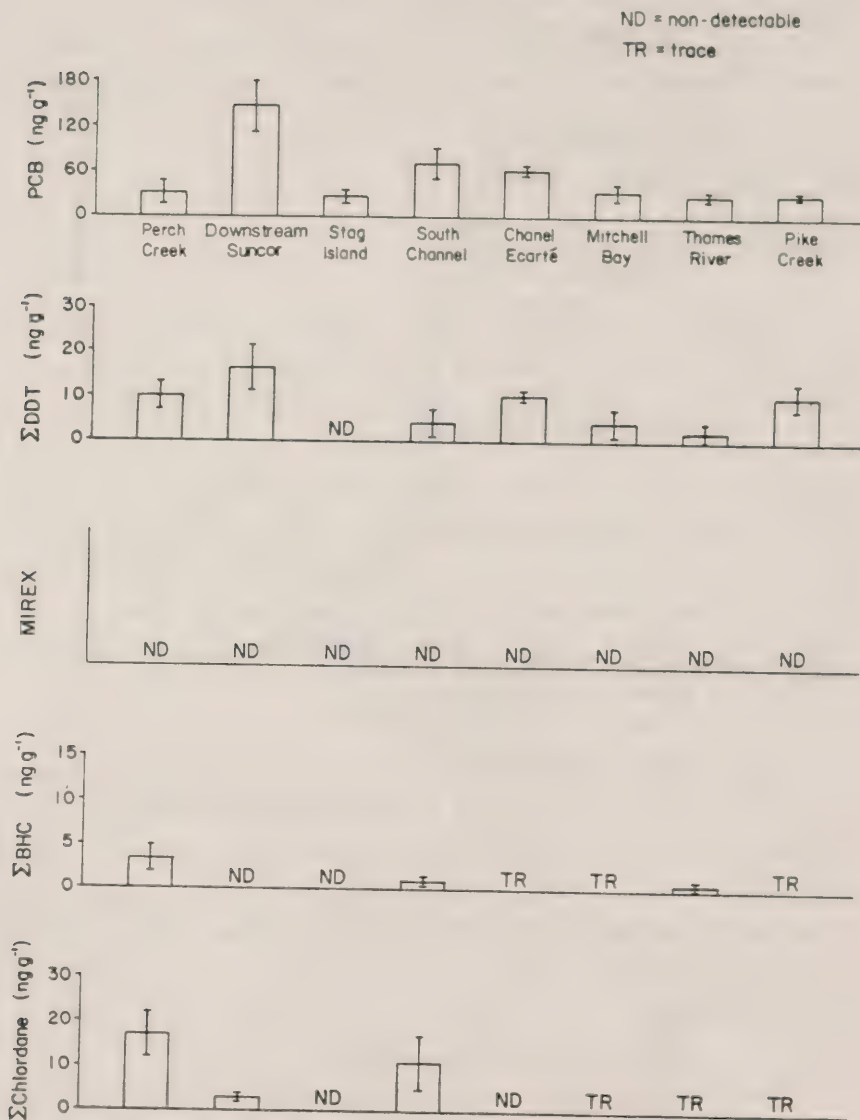


Figure 3.50 Organochlorine residues in 1982/1983 young-of-the-year spottail shiner collections from Lake Huron, the St. Clair River and Lake St. Clair (means \pm 95% C.L.).

PCB, Σ DDT, mercury and chlordane residue trends in young-of-the-year spottail shiners from Lake St. Clair at Pike Creek.

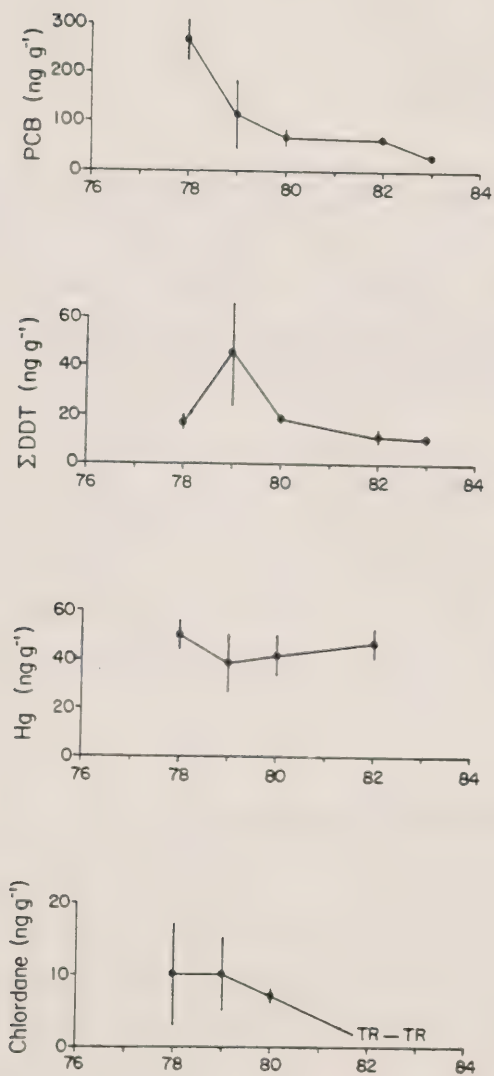


Figure 3.51 PCB, DDT, mercury and chlordane residue trends in young-of-the-year spottail shiners from Lake St. Clair at Pike Creek.

Pike Creek have decreased significantly ($P < 0.01$) over a four-year period.

Chlorinated Aromatics

Hexachlorobenzene residues were elevated (231 ng/g) in spottail shiner collections from Suncor (Fig. 3.52). These residue accumulations were well above the Lake Huron control and well over the typical residue levels found in Great Lakes spottail-shiners, which generally range from not-detected to 10 ng/g. Similarly, octachlorostyrene accumulations of 560 ng/g in the Suncor collections exceeded the not-detected to 6 ng/g range commonly found at other lower Great Lakes sites. These residue accumulations suggest active inputs of hexachlorobenzene and octachlorostyrene to the St. Clair River. Elevated octachlorostyrene residues in the St. Clair River spottail shiners extend to the Chenal Ecarte (28 ng/g) and the south channel (95 ng/g) estuaries in Lake St. Clair whereas the impact of hexachlorobenzene appears to be more localized.

Polycyclic Aromatic Hydrocarbons (PAHs)

A total of 19 individual isomers were determined to assess the PAH content in young-of-the-year spottail shiners from the St. Clair River at Suncor. Of the 15 sites analyzed throughout the Great Lakes, PAH accumulations at Suncor ranked third highest with 4614 pg/g. At Suncor, 42% of the total PAHs in the shiners were isomers with known or suspected carcinogenic characteristics, the highest percentage found at any of the 15 Great Lakes sites.

Chlorinated aromatic residues in 1982/83 young-of-the-year spottail shiner collections from Lake Huron, the St. Clair River and Lake St. Clair (means \pm 95% C.L.)

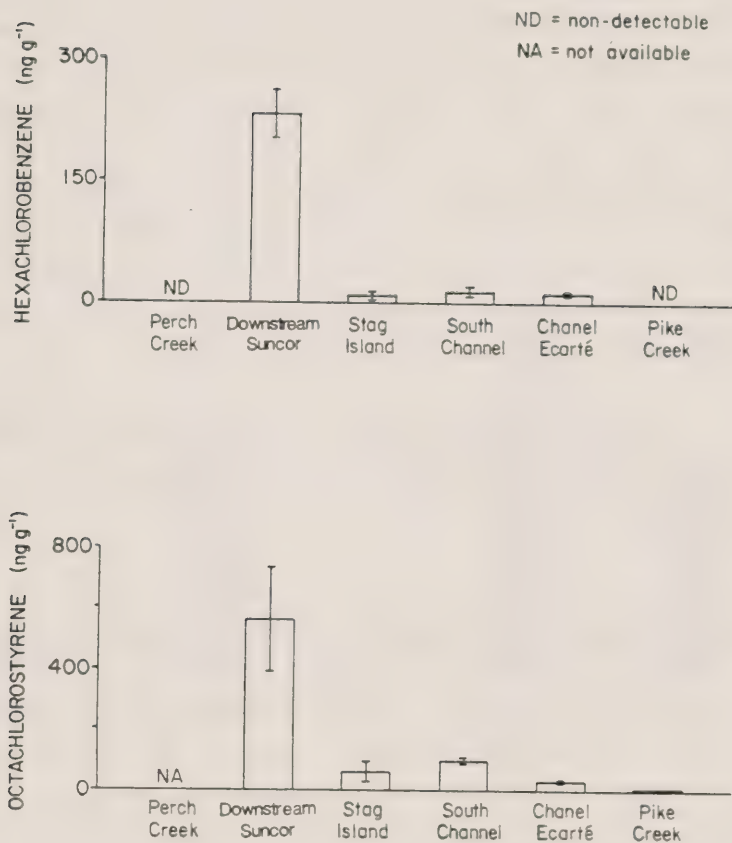


Figure 3.52 Chlorinated aromatic residues in 1982/1983 young-of-the-year spottail shiner collections from Lake Huron, the St. Clair River and Lake St. Clair (means \pm 95% C.L.).

Perchloroethylene

Perchloroethylene residues in emerald shiners appeared to increase with time following the spill on August 12, 1985, at Dow Chemical. Whereas perchloroethylene residues at Suncor and Port Lambton were 200 ng/g, and 19 ng/g, respectively, four weeks after the spill, the residues seven weeks after, at the same sites, were found to be 380 ng/g and 320 ng/g (Fig. 3.53). The highest perchloroethylene residue accumulations were found at Lambton Generating Station, some 20 km downstream from Dow Chemical and at Mitchell Bay in Lake St. Clair. While these increases appeared to be real, the data are not supported statistically due to lack of replicate analyses.

It should be noted that perchloroethylene residues in emerald shiners upstream from the Sarnia industrial complex were non-detectable on both sampling occasions.

Polychlorinated Dibenzo-p-Dioxins (PCDD) and Dibenzofurans (PCDF)

Dioxin tetra-congener (T_4 CDD) residues were not detected in any of the collections analyzed. Therefore, it may be concluded that biologically available 2,3,7,8-TCDD was not present in the water of the upper St. Clair River. Residues for the hepta-congener (H_7 CDD) were slightly elevated at Suncor and Stag Island when compared with the control (Fig. 3.54).

The spatial distribution data of the TCDF residues indicate that residues in the control fish were similar to those of the downstream collections at Suncor and Stag Island. Considering the similarities in residue concentrations and the number of

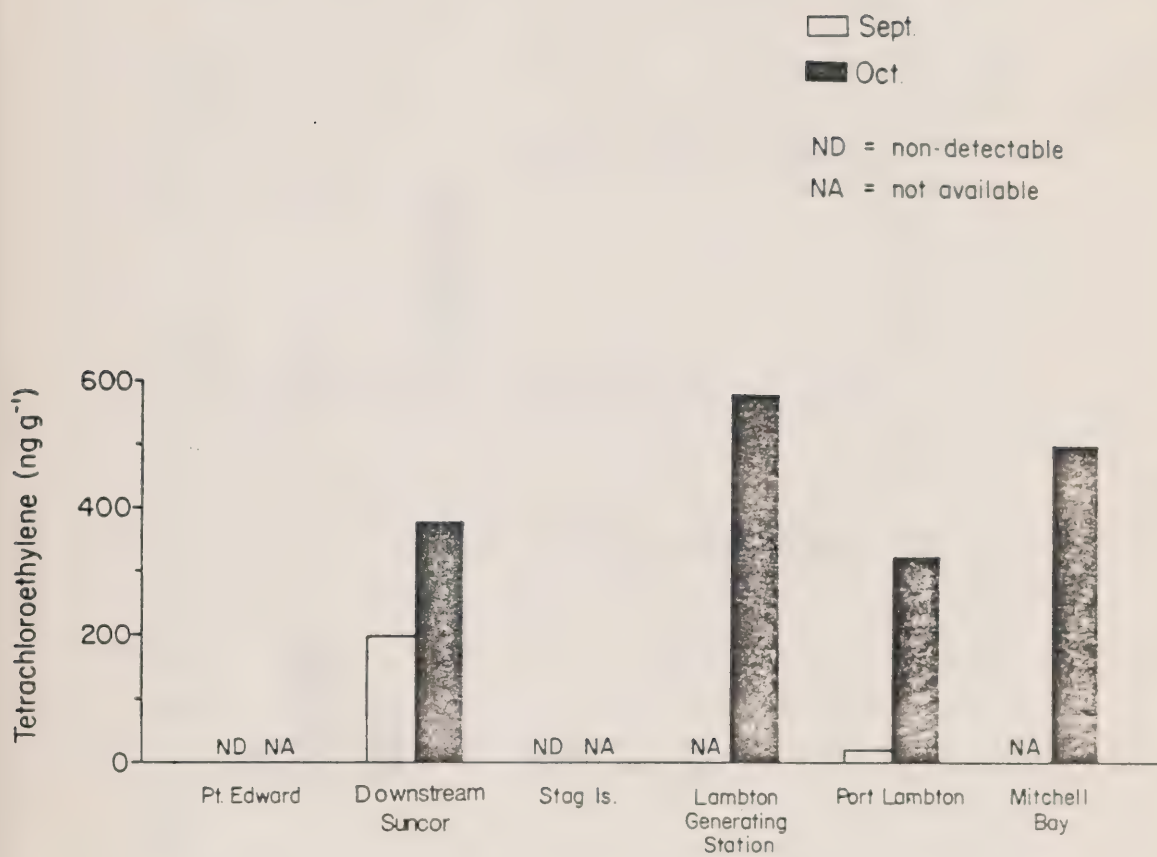


Figure 3.53 Tetrachloroethylene residues in juvenile emerald shiners from the St. Clair River on September 11 and October 12, 1985.

Figure : Polychlorinated dibenzo-p-dioxin and dibenzofuran residues (pg g^{-1}) in juvenile emerald shiners from the St. Clair River in 1985 (ND = non-detectable, detection limit = 10 pg g^{-1}).

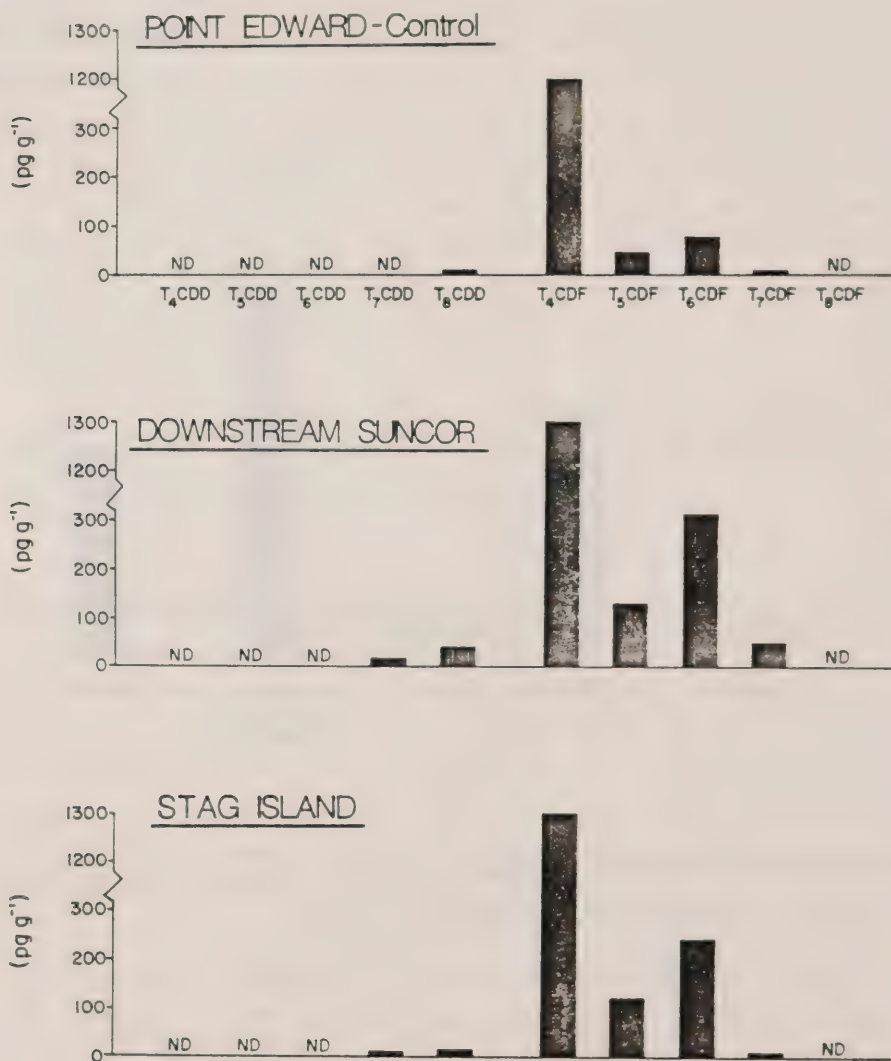


Figure 3.54 Polychlorinated dibenzo-p-dioxin and dibenzofuran residues (pg g^{-1}) in juvenile emerald shiners from the St. Clair River in 1985. (ND = non-detectable, detection limit = 10 pg g^{-1})

identified isomers, it may be concluded that TCDF inputs originated from Lake Huron and not from the industries.

Penta (P_5 CDF) and hexa-congener (H_6 CDF) residues were elevated in the Suncor and Stag Island collections compared with the control collection. However, since this observation was based on a single analysis, the significance of these differences cannot be determined.

Mercury

Mercury in spottail shiners from the South Channel and Mitchell Bay collections was significantly ($P 0.05$) elevated when compared to the Lake Huron control at Perch Creek (Fig. 3.55). Elevated mercury residues in the St. Clair River and Lake St. Clair are probably related to mercury inputs from Dow Chemical during the 1960s. Mercury concentrations in spottail shiners from Lake St. Clair at Pike Creek have remained virtually unchanged over a four-year (1978 to 1982) interval (Fig. 3.51).

Lead

Significant ($P 0.01$) elevations of total lead were found in young-of-the-year yellow perch collections at Corunna (Fig. 3.56). The collection site on the eastern bank of the St. Clair River was downstream from Ethyl Corporation of Canada, and the massive residue accumulations suggest active lead inputs to the River (DOE, 1986).

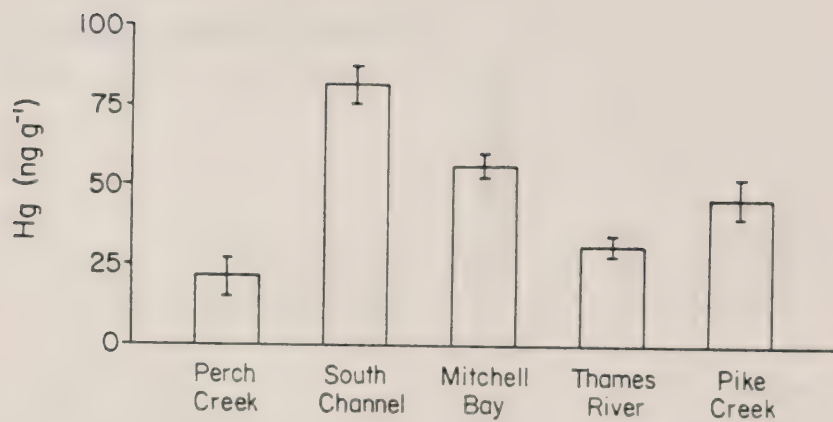


Figure 3.55 Mercury residues in 1982/1983 young-of-the-year spottail shiner collected from Lake Huron, the St. Clair River and Lake St. Clair (means \pm 95% C.I.)

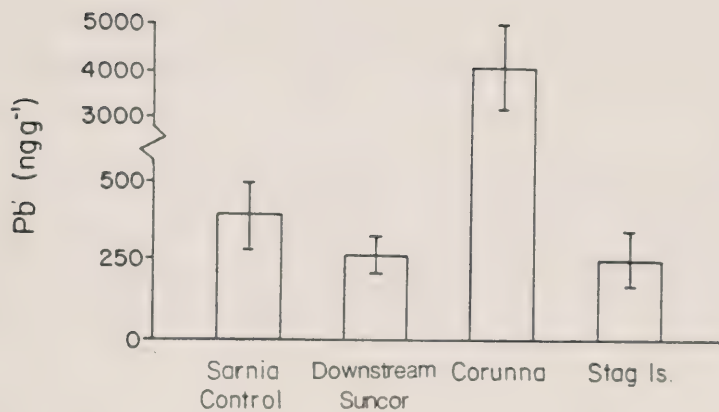


Figure 3.56 Total lead residues in young-of-the-year yellow perch from the St. Clair River in 1984 (means \pm 95% C.L.).

In summary, juvenile fish surveys have identified elevated hexachlorobenzene, octachlorostyrene and PCBs in the St. Clair River downstream from the industrial complex at Sarnia, and elevated lead at Corunna. Considering the magnitude of the residue accumulations it may be concluded that active inputs of biologically available hexachlorobenzene, octachlorostyrene and lead exist to the River.

Although the origins of polycyclic aromatic hydrocarbons and polychlorinated dibenzofurnas in the St. Clair River remain undetermined, there is concern about the high carcinogen content in PAH residues and the potential for 2,3,7,8-TCDF being present in unacceptable concentrations.

Temporal trend data show that PCB and total chlordane residues in young-of-the-year spottail shiners at Pike Creek have decreased significantly ($P < 0.01$) over a four year (1978 to 1982) interval, whereas total DDT and mercury levels have changed little.

RECOMMENDATION

It is recommended that additional efforts in analytical development for the analysis of PAH and PCDF to the isomer level for young-of-the-year spottail shiners in the St. Clair River system be provided to enhance source identification and permit expanded and more meaningful residue data evaluation.

CONTAMINANTS IN LAKE ST. CLAIR SPORT FISH 1970 TO 1984

The Ontario government has collected and analyzed at least 11 526 individual fish of 19 different species from Lake St. Clair in the period 1970 to 1984. Studies are ongoing with at least 200 fish of 10 species collected annually. Samples are taken by the Lake St. Clair Assessment Unit of Ministry of Natural Resources and analysed by the MOE. All data have been assessed using Health and Welfare Canada guidelines for human consumption. Consumption advice on fish from Lake St. Clair has been routinely made available to the public by means of the "Guide to Eating Ontario Sport Fish," which has been published annually since 1978 (MOE/MNR, 1985).

Mercury in Lake St. Clair Fish

An estimated 100 000 kg of mercury was lost to the St. Clair River by the Dow Chemical Co. chlor-alkali plants in the 1950s and 1960s. As late as September 1969, up to 31 kg/day was still being released. By May 1970, losses were less than 0.4 kg/day. Later, discharges ceased altogether (Neary, 1981).

Mercury levels in the edible portion (skinless, boneless fillet) of Walleye Stizostedion vitreum (Mitchell) have shown a steady decline since 1970 (Fig. 3.57). The current average level is 30% of the 1970 value. At present, walleye up to 45 cm (18") contain less than 0.5 ppm mercury and are suitable for unlimited consumption.

The mercury level in northern pike, Esox lucius (Linnaeus) fillets in 1970 was about double that of the walleye at the time

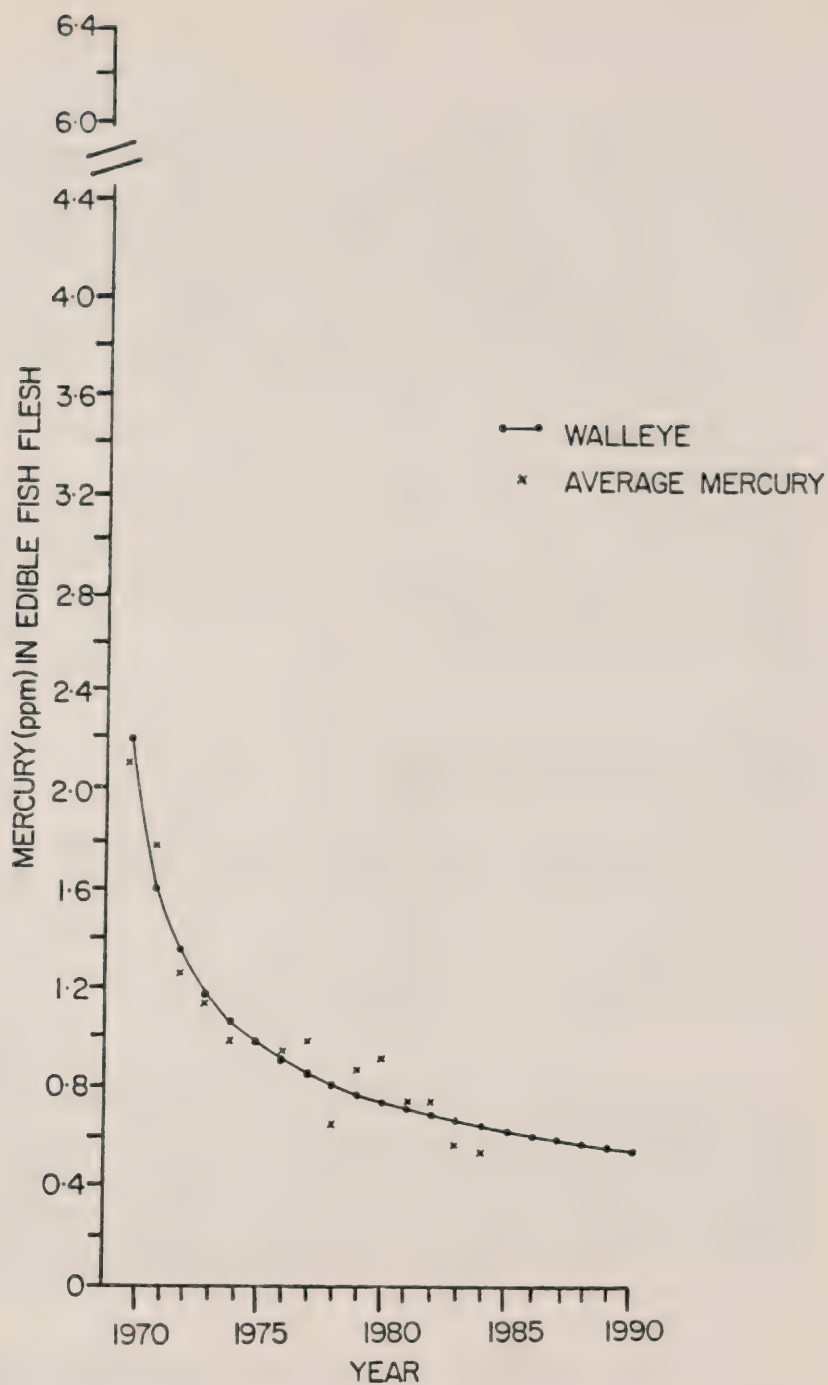


Figure 3.57 Mercury in Lake St. Clair fish.

(Fig. 3.58). Levels are now less than 25% of the 1970 values and pike up to 45 cm (18") contain less than 0.5 ppm mercury and are suitable for unlimited consumption.

White bass Morone chrysops (Rafinesque) mercury levels are less than 20% of the 1970 values (Fig. 3.58) and specimens up to 30 cm (12") contain less than 0.5 ppm.

Yellow perch, Perca flavescens (Mitchell), had lower mercury levels in 1970 than white bass, pike or walleye. As of 1984, mercury levels were about 20% of the initial measurements and perch up to 25 cm (10") contain less than 0.5 ppm (Fig. 3.58).

Channel catfish, Ictalurus punctatus (Rafinesque), a shallow water omnivore (in contrast to the four previously discussed predatory species) shows similar declines in mercury levels over time in spite of its somewhat different feeding habits. Specimens up to 55 cm (22") in length contain less than 0.5 ppm mercury (Fig. 3.59a).

Carp, Cyprinus carpio (Linnaeus), another shallow water omnivore shows an identical pattern and degree of decline in mercury levels as the channel catfish. Similarly, carp up to 55 cm (22") contain less than 0.5 ppm mercury and are, therefore, suitable for unlimited consumption (Fig. 3.59b).

PCB in Lake St. Clair Fish

With the exception of two species, carp and channel catfish, PCB levels in the edible portions of Lake St. Clair fish have not exceeded the Canadian federal guideline of 2.0 ppm.

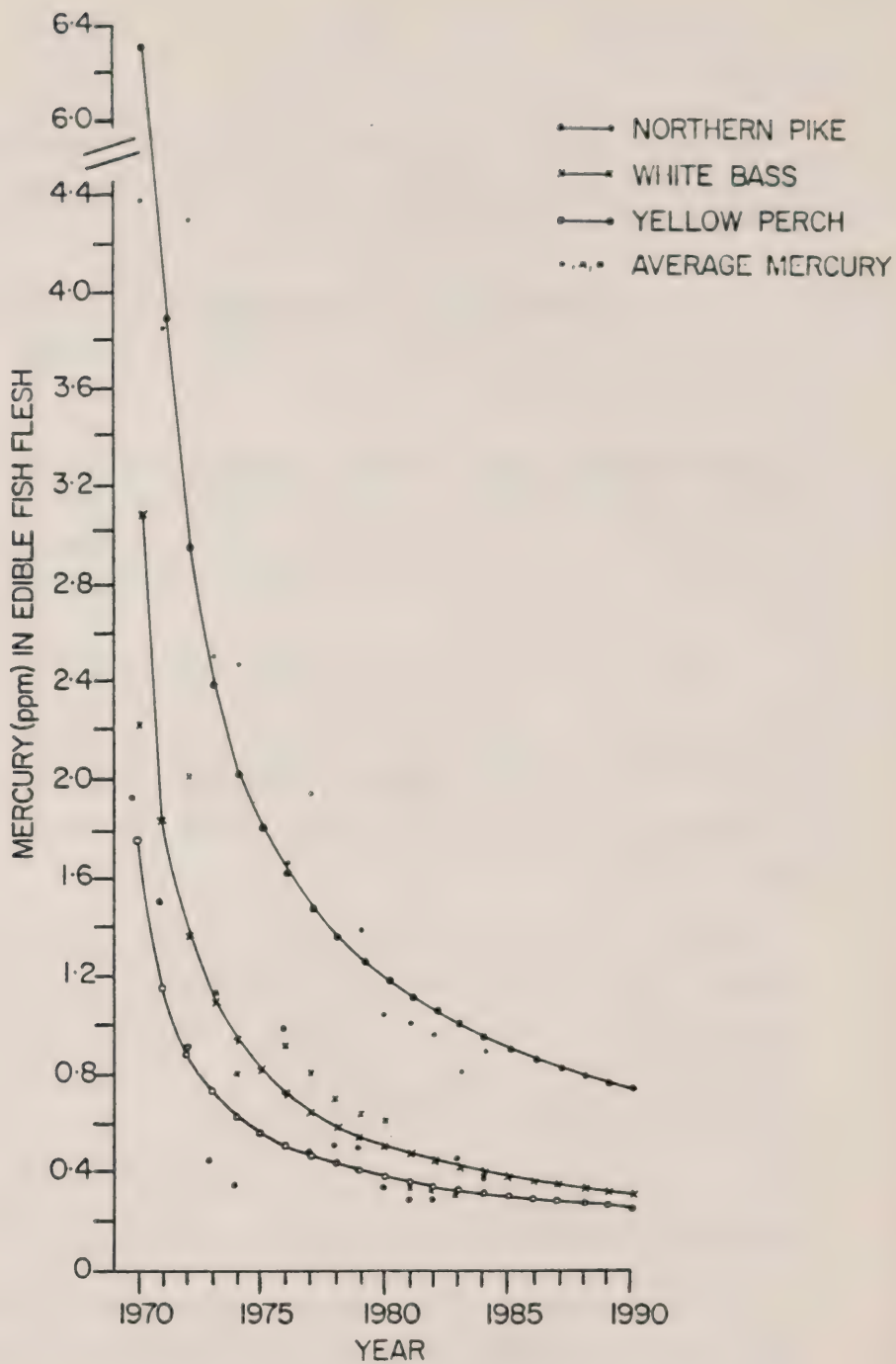


Figure 3.58 Mercury in Lake St. Clair fish.

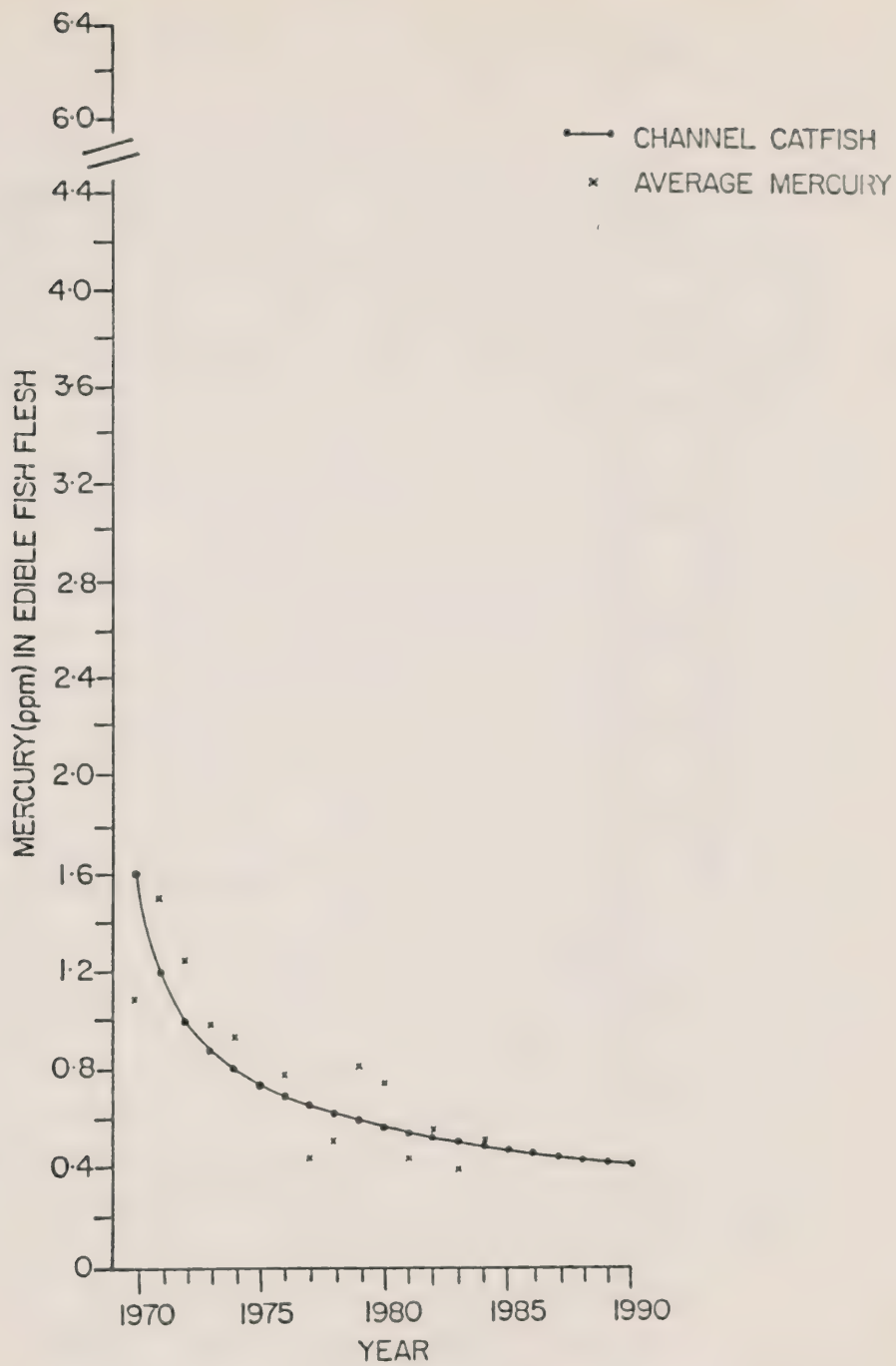


Figure 3.59a Mercury in Lake St. Clair fish.

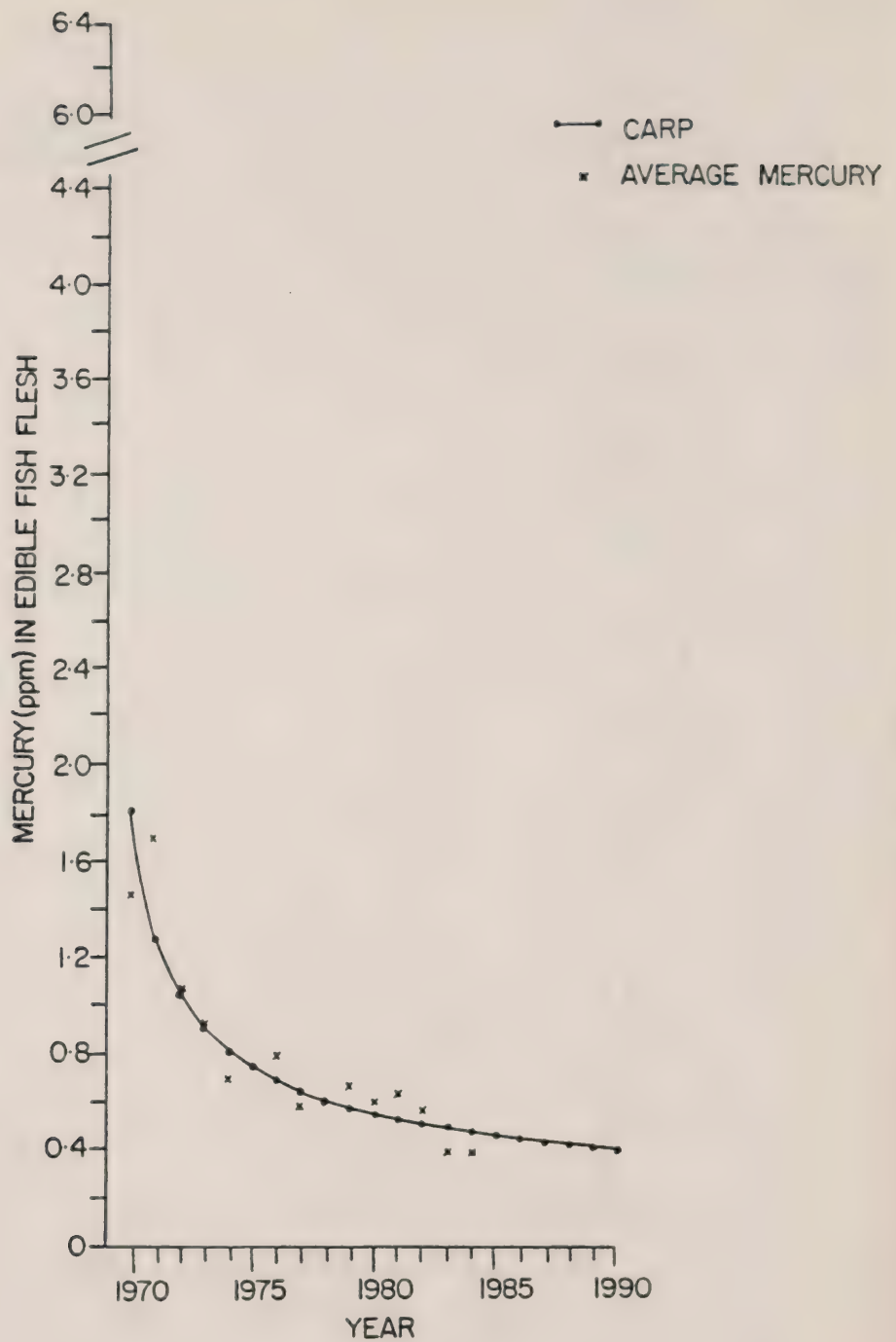


Figure 3.59b Mercury in Lake St. Clair fish.

The data for walleye (Fig. 3.60) show variable but declining values. The variability may result from discontinuous or "patchy" exposure to this substance. The perch data show low, slightly declining levels from 1977 through 1983. In Figure 3.61, PCB declines in white bass are more clearly seen. Average values of PCB in carp have also declined since first measured in 1976. At one time the "Guide to Eating Ontario Sport Fish" advised limits on consumption of larger sizes of carp. This is no longer necessary.

PCB in Channel Catfish have been variable due to the size variability. However, PCB levels average 50% of those in 1976 and Catfish up to 55 cm (22") are suitable for unlimited consumption. Those from 55 to 75 cm (22" to 30") exceed 2.0 ppm PCB. They are the only Lake St. Clair fish to do so.

DDT in Lake St. Clair Fish

Figures 3.62 and 3.63 show the average values of DDT and the best-fit geometric regression curves. In the period of measurement DDT has never exceeded the federal (Health and Welfare Canada) maximum allowable level of 5 ppm (5000 ppb) in any species tested (13 species). The curves for DDT show the same species relationship as the PCB data; channel catfish and carp are highest, white bass and walleye are similar and perch is the lowest (most values in perch are at or near the detection limit).

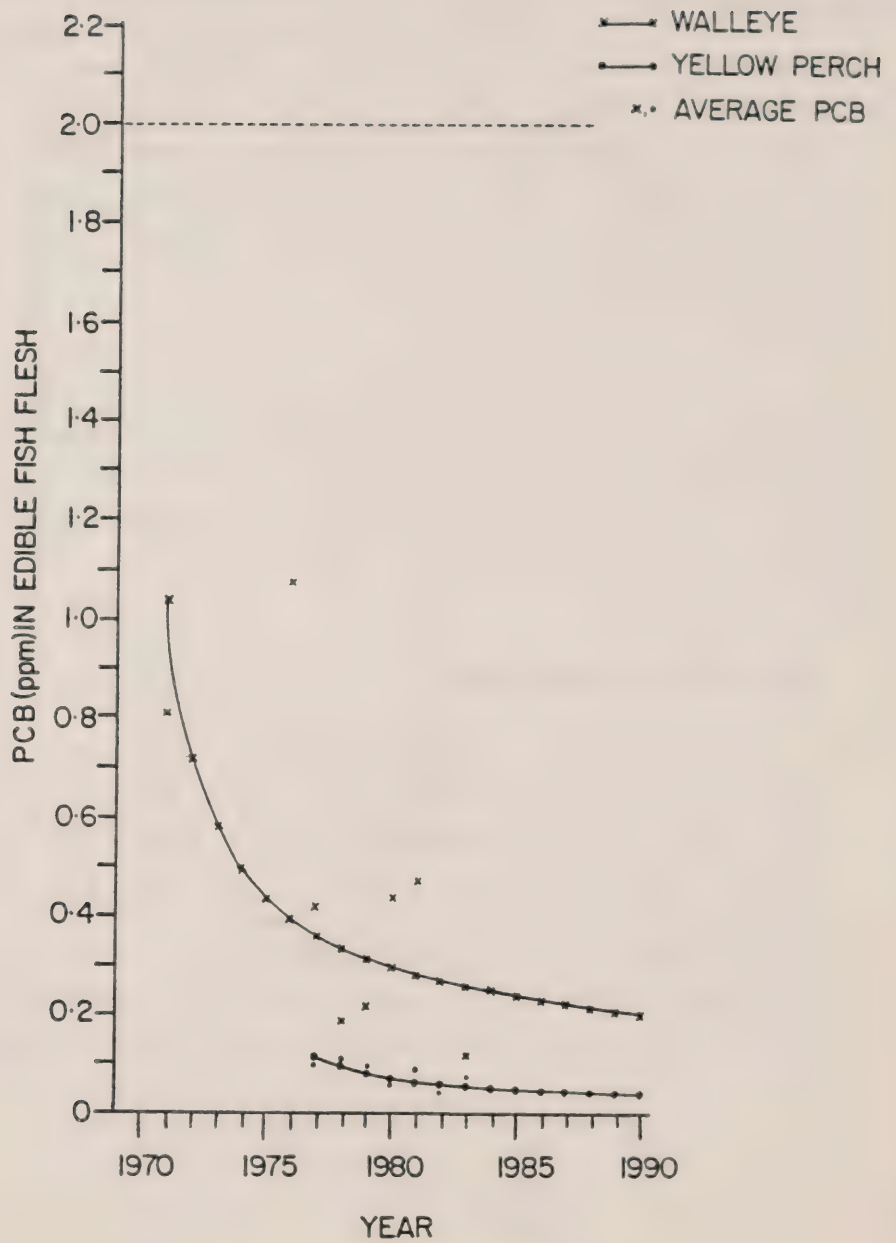


Figure 3.60 PCB in Lake St. Clair fish.

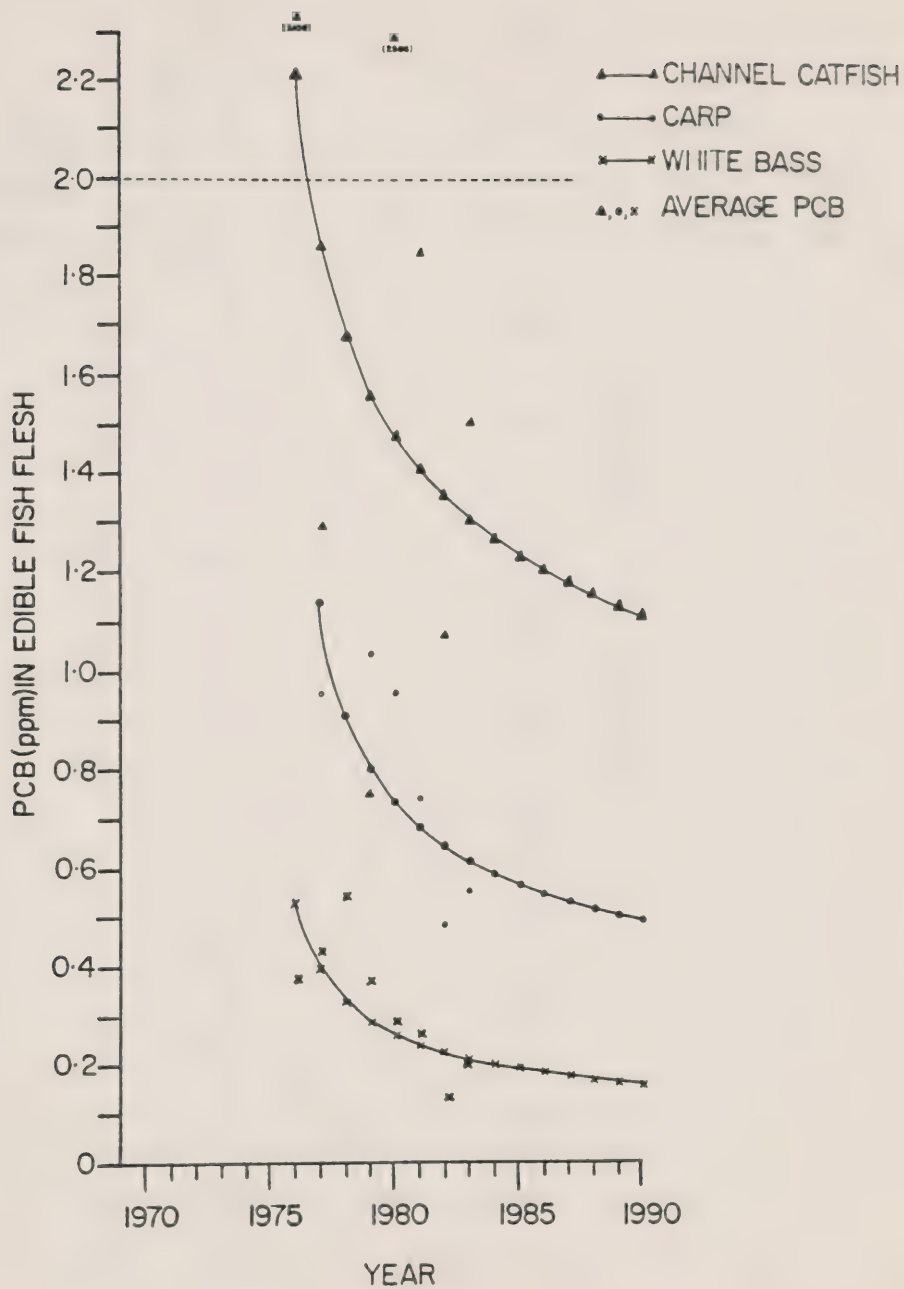


Figure 3.61 PCB in Lake St. Clair fish.

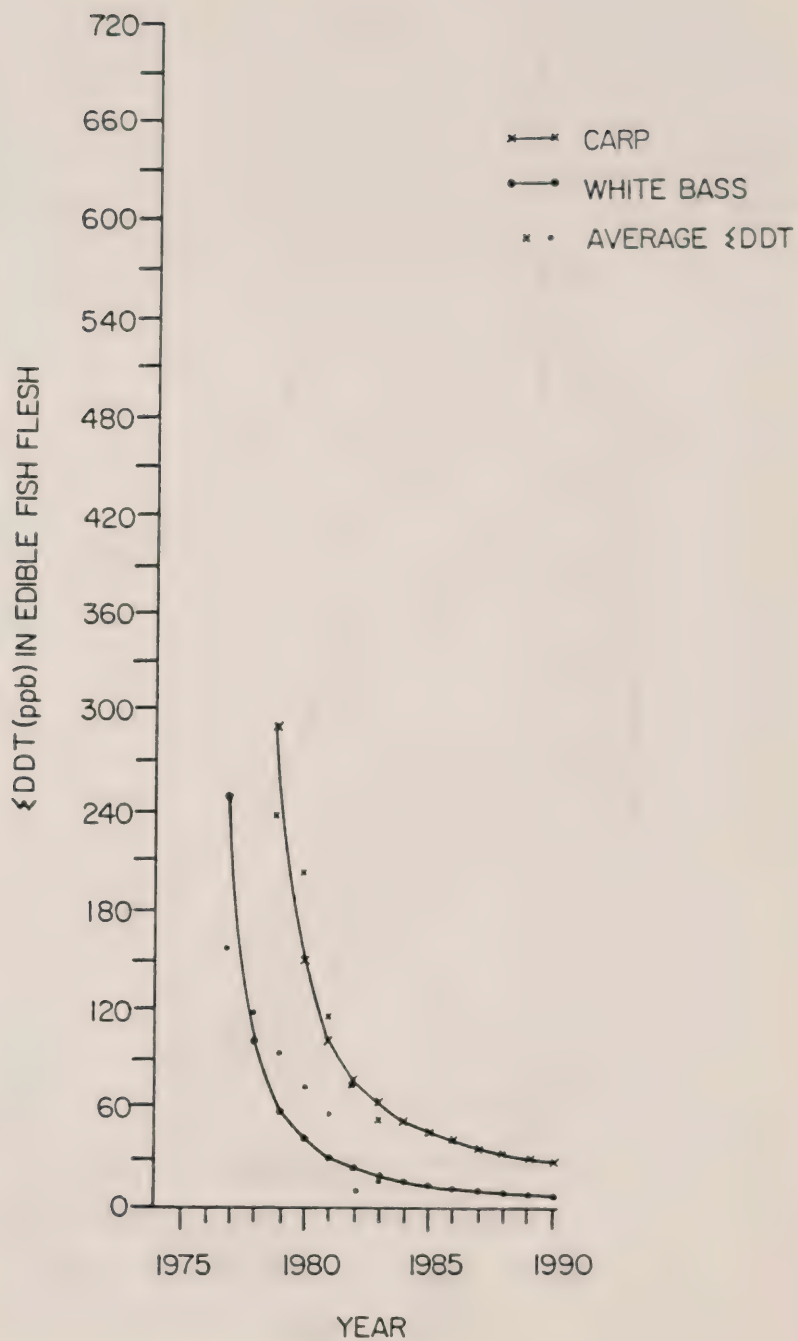


Figure 3.62 DDT in Lake St. Clair fish.

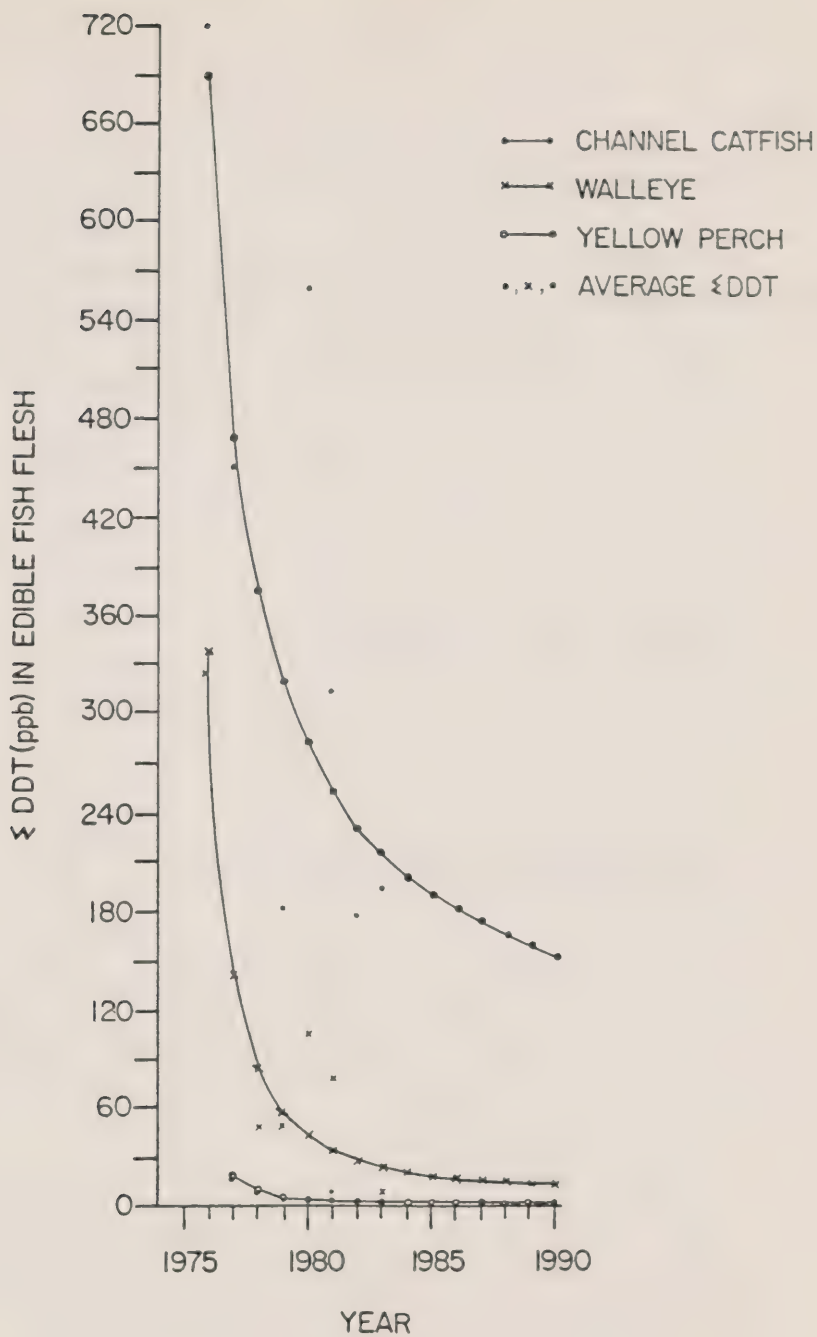


Figure 3.63 DDT in Lake St. Clair fish.

Chlordane in Lake St. Clair Fish

Figure 3.64 gives the average values and best-fit regression curves for chlordane in channel catfish, carp and white bass. Gradual restriction in the use of chlordane began in the late 1970s and this is reflected by the data. There is no published tolerance level for chlordane in fish flesh in Canada. A guideline of 300 ppb has been used in the U.S.A. Current values do not approach this criterion.

Lindane in Lake St. Clair Fish

Figure 3.65 shows the near detection limit values of lindane in carp.

Hexachlorobenzene in Lake St. Clair Fish

Figure 3.66 compares the average values of HCB detected in Lake St. Clair channel catfish. 1982 and 1983 values are about 50% of those recorded in 1981. In comparison, HCB levels in southern Lake Huron catfish were much lower than Lake St. Clair specimens.

Figure 3.67 gives similar data for carp from both locations. Values in Lake St. Clair specimens are again lower in 1982 and 1983 than in 1981. In 1983 Lake Huron samples of carp were higher in HCB than the Lake St. Clair specimens.

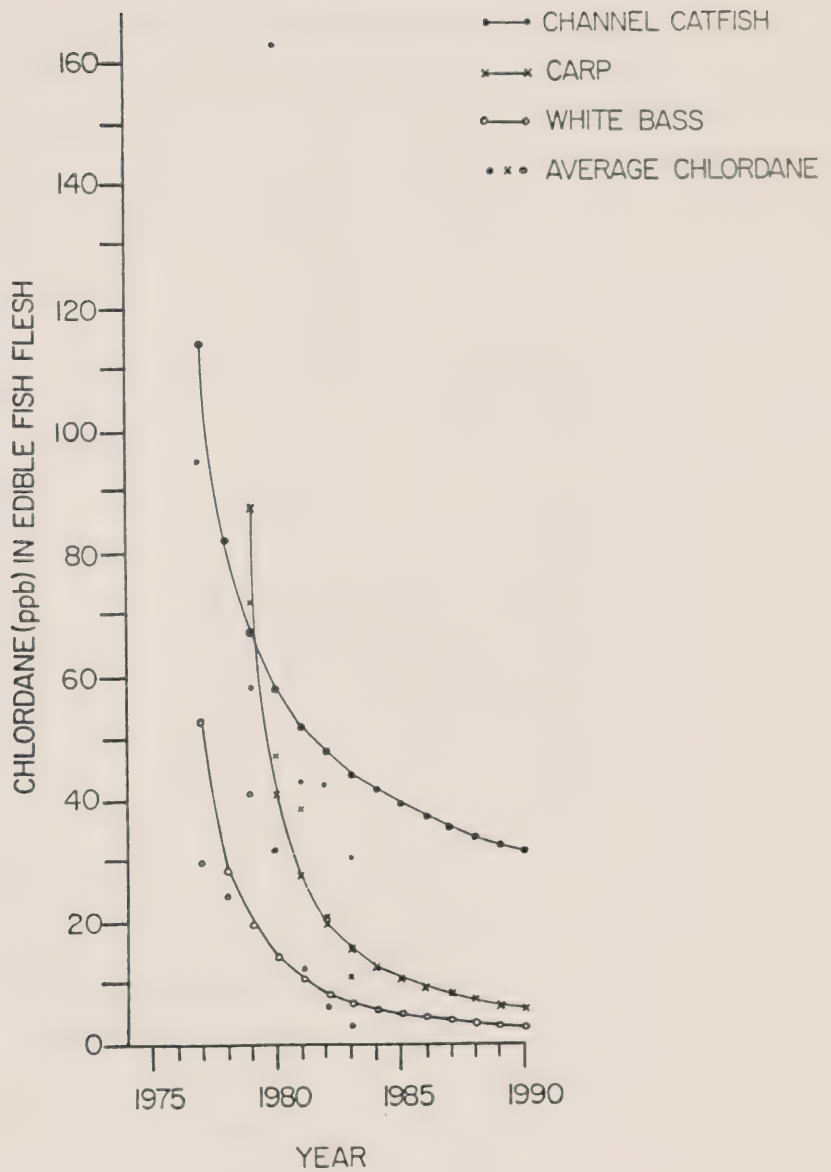


Figure 3.64 Chlordane in Lake St. Clair fish.

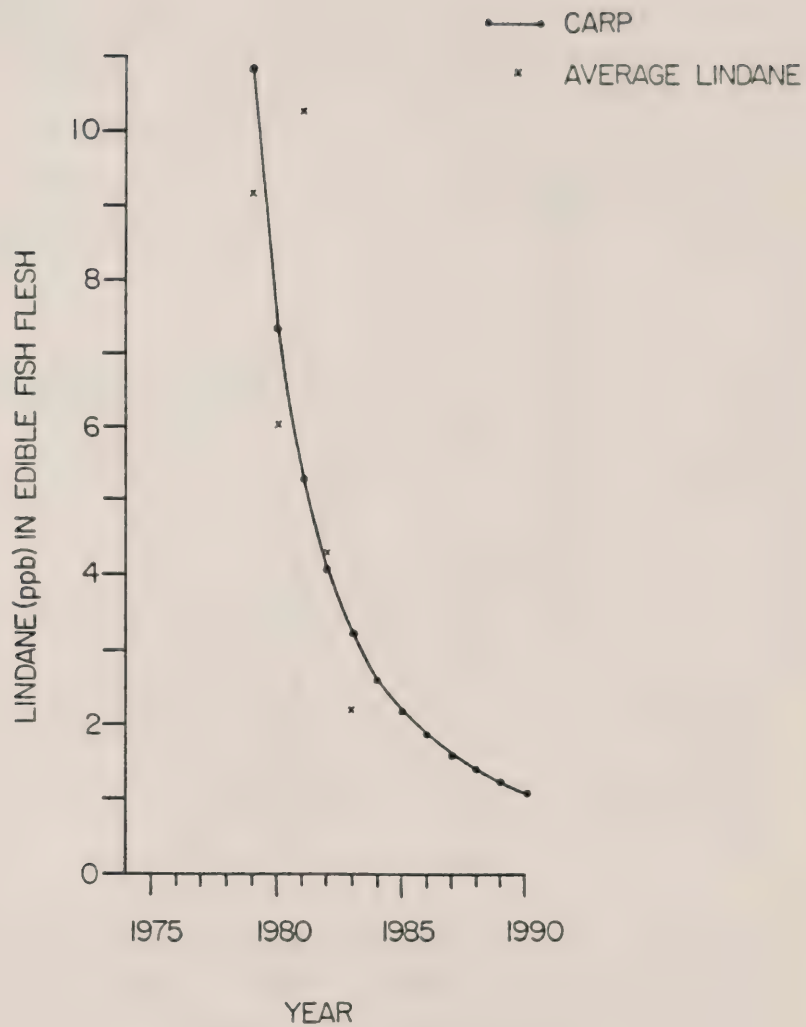


Figure 3.65 Lindane in Lake St. Clair fish.

LAKE ST. CLAIR AND S. LAKE HURON

HCB IN CHANNEL CATFISH

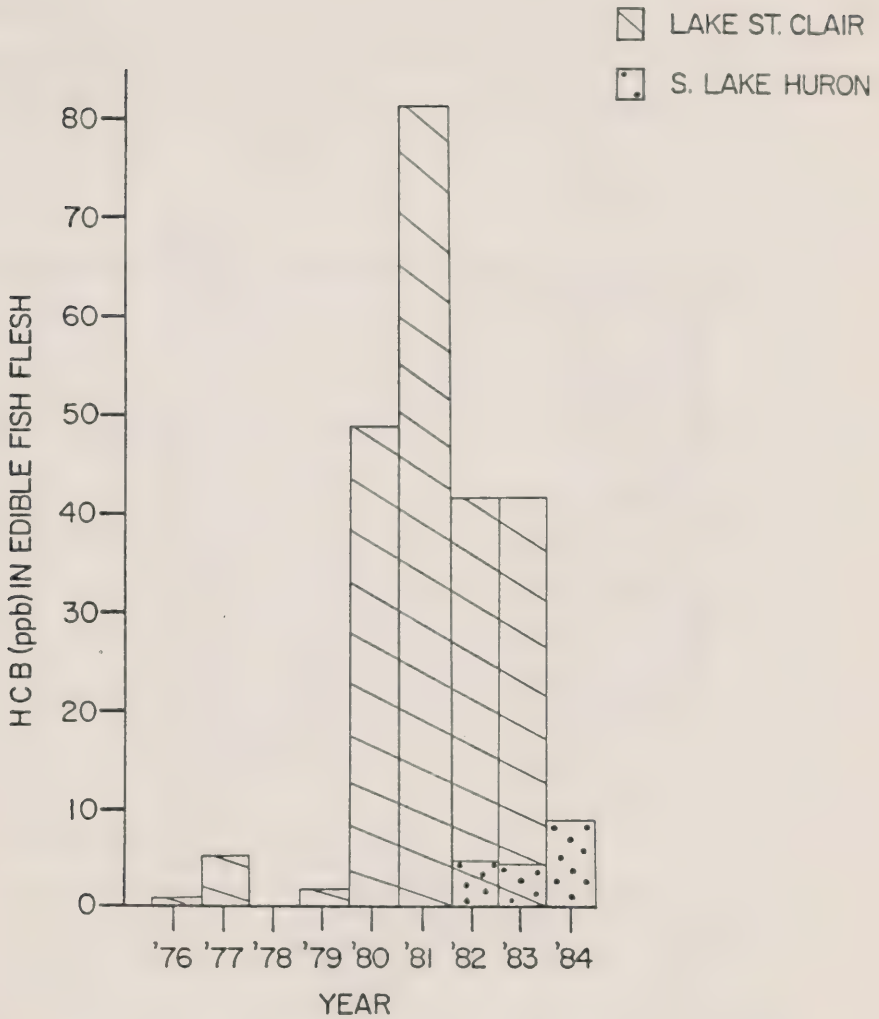


Figure 3.66 HCB's in channel catfish from Lake St. Clair and S. Lake Huron.

LAKE ST. CLAIR AND S. LAKE HURON

HCB IN CARP

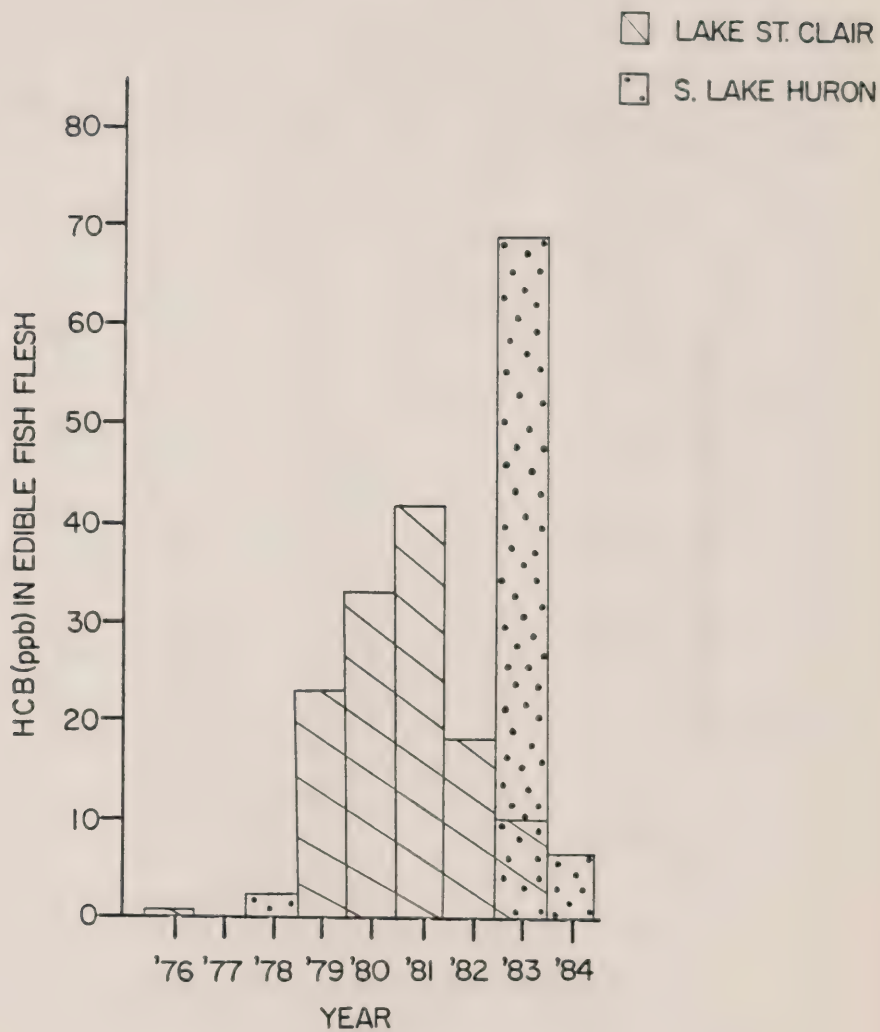


Figure 3.67 HCB's in carp from Lake St. Clair and S. Lake Huron.

Octachlorostyrene in Lake St. Clair Fish

Figures 3.68 and 3.69 present the limited data for OCS in channel catfish and carp. As with HCB, channel catfish from Lake St. Clair have higher levels than do Lake Huron specimens. With carp, the reverse is the case.

Chlorinated Dioxins and Dibenzofurans in Lake St. Clair Fish

Three species of fish collected in 1982 from Lake St. Clair were analysed for 2,3,7,8-TCDD and TCDD/TCDF or PCDD/PDCF. The dioxin 2,3,7,8-TCDD was detected in channel catfish (mean of 0.89 ppt) and carp (mean of 0.6 ppt). No 2,3,7,8-TCDD was detected in walleye. This information was sent to Health and Welfare Canada in May 1984. The maximum allowable level of this dioxin in fish flesh has been set by Health and Welfare Canada at 20 ppt. Assessment of the other dioxins and dibenzofurans by the MOE proposed equivalent-to-2,3,7,8-TCDD method (MOE, Sept. 1985) is given in Table 3.19. Carp collected from the St. Clair River at Corunna by Great Lakes Fisheries Research Branch (DFO, 1986)

Table 3.19 PCDD/PCDF Equivalent to 2,3,7,8-TCDD Values in 1982 Lake St. Clair Sport Fish

Species	Number	2378-TCDD Equivalent (includes 2378-TCDD) ppt	2378-TCDD Mean and Range ppt
Carp	10	1.7	0.6 (ND - 2)
Channel catfish	9	1.8	0.90 (ND - 4.7)
Walleye	10	1.8	ND

Large numbers of Lake St. Clair fish samples for dioxins and dibenzofurans are presently undergoing analysis in the MOE Dioxin Laboratory.

LAKE ST. CLAIR AND S. LAKE HURON

OCS IN CHANNEL CATFISH

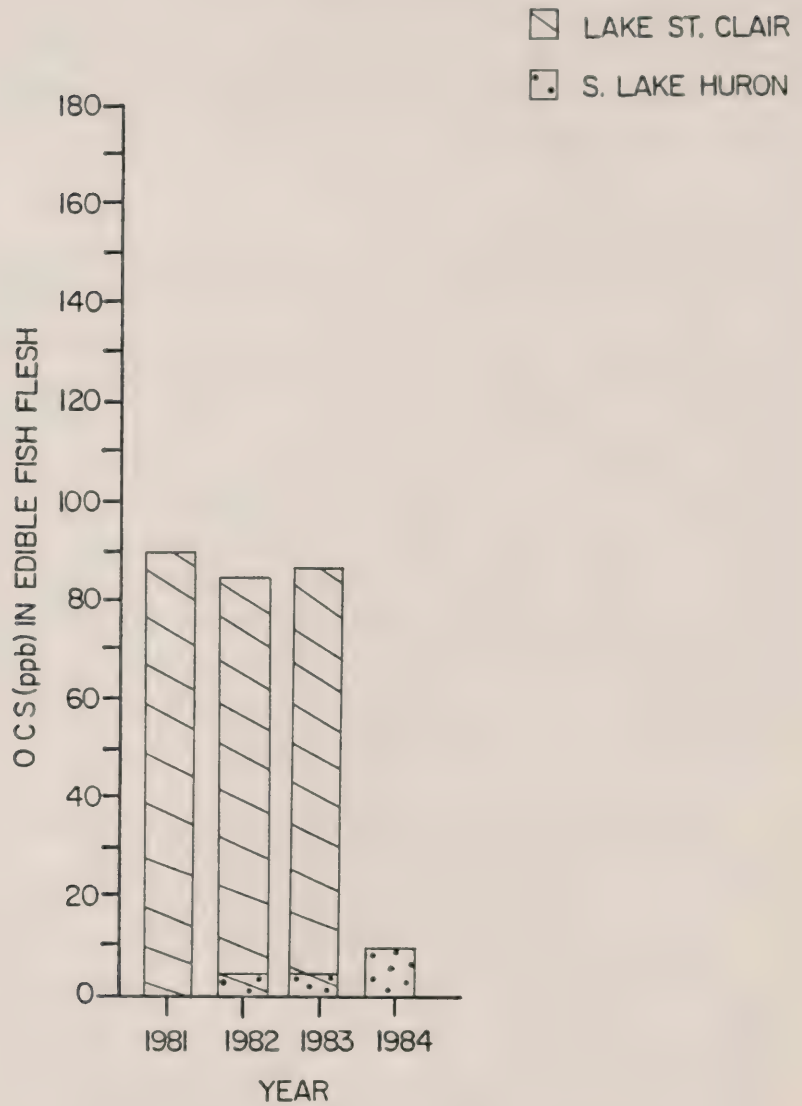


Figure 3.68 Organochlorines in channel catfish from Lake St. Clair and S. Lake Huron.

LAKE ST. CLAIR AND S. LAKE HURON

OCS IN CARP

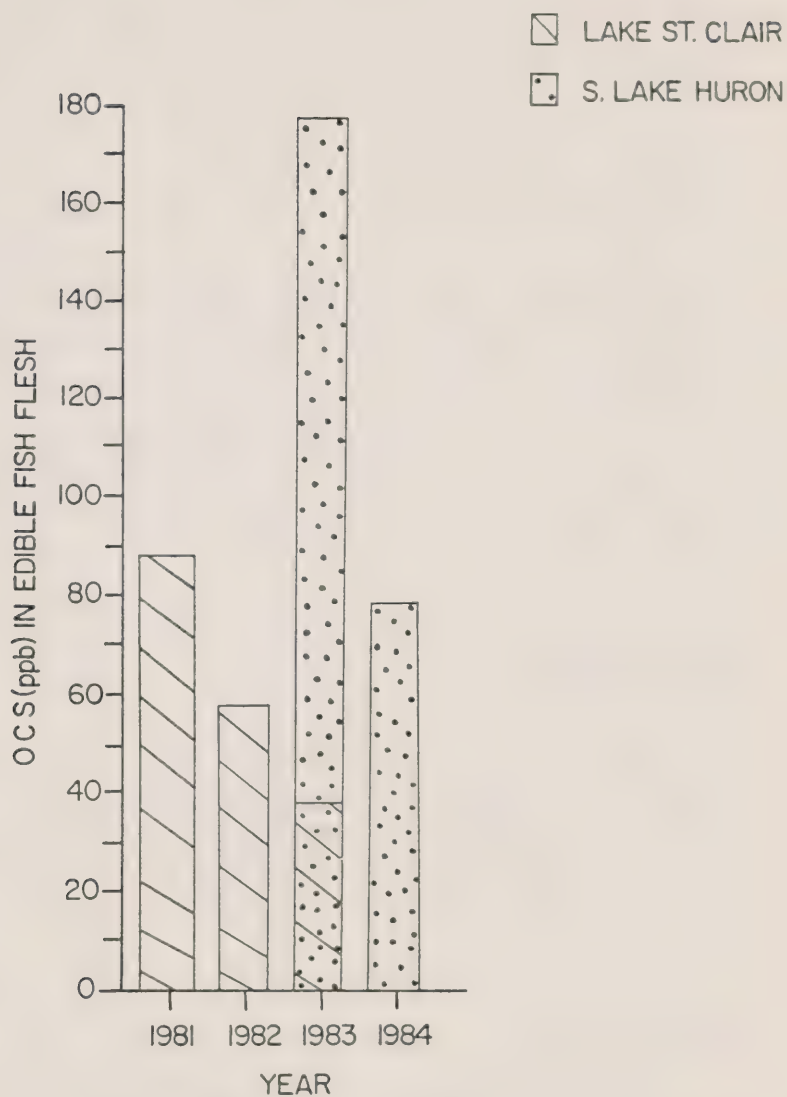


Figure 3.69 Organochlorines in carp from Lake St. Clair and S. Lake Huron.

were found to have 4 ppt and 5 ppt of 2,3,7,8-TCDD and 2,3,7,8-TCDF, respectively. At the present time, the source of chlorinated dioxins and benzofurans is unknown.

Lead in St. Clair River Fish

Table 3.20 shows the data for total lead obtained in a 1983 survey of edible portions of sport fish collected at Stag Island, immediately downstream from the Ethyl Corp. discharge. These levels did not require any limitation on consumption of sport fish because of lead. In 1985, large numbers of fish (257) of six species were collected in the St. Clair River for further assessment of the Ethyl Corp. discharge (see also DOE, 1986). These samples are awaiting analysis.

Other Compounds

Table 21 shows the results of whole fish analysis of a gizzard shad Dorosoma cepedianum (Lesueur) and a channel catfish. Assessment of the feasibility of routinely monitoring the chlorinated benzenes, substituted phenols and PAH's in edible portions of sport fish is presently under study.

RECOMMENDATION

Additional species of sport fish from Lake St. Clair and Lake Huron (control) should be analyzed for chlorinated benzenes, dioxins, furans, PAHs and substituted phenols, given the importance of the recreational fishery and the high public utilization of fish from this lake.

Table 3.20 St. Clair River (Stag Island) Lead Summary

Location	Species	No.	Length (cm)			Weight (g)			Lead (ppm)		
			Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.
St. Clair River Stag Island 4253/8228 Sarnia Twp. Lambton Co. 1983	Rock Bass	24	16.1	11.8	21.9	102	33	262	0.15	0.11	0.20
	Yellow Perch	16	24.1	15.7	32.3	239	40	560	0.22	0.11	0.79
	Carp	2	50.2	47.2	53.2	2137	1605	2668	1.21	0.23	2.2
	Rainbow Trout	5	27.5	19.3	48.2	397	75	1555	0.134	0.13	0.14

Table 3.21 Analytical Data on Fish Collected from Lake St. Clair
(ng/g)

Sample Identification	LSC	MOEF7
Species	GS	CC
Location	St. Clair	St. Clair
<u>Compound</u>		
Alpha-BHC	ND	13.0
Hexachlorobenzene	100.0	1.8
p,p'-DDE	64.0	570.0
p,p'-DDD/o,p'-DDT	32.0	140.0
p,p'-DDT	ND	110.0
DDMU	ND	ND
Chlordanes	ND	75.0
Monochlors	ND	170.0
Dichlorobenzene	ND	140.0
Dieldrin	ND	ND
Naphthalene	ND	4.6
Phenanthrene	ND	4.3
Fluoranthene	ND	1.0
Pyrene	ND	0.3
PCB	*	***
CA-phenol	ND	ND
Unkn.S (M.W.#180)	32.0	14.0
Unkn.CL2 (M.W.#190)	ND	ND
<u>Possible Natural Compounds</u>		
Benzoic acid	ND	ND
Benzene acetic acid	4100.0	ND
Benzene propionic acid	1900.0	ND

* = Less than 500 ng/g.

** = Greater than 1000 ng/g.

Species: CC = channel catfish GS = gizzard shad

CLAM BIOMONITORING STUDIES

Introduced clams (Elliptio complanatus) have been used as biomonitors to assess the distribution, biological availability and source areas of a number of chlorinated organic contaminants in the St. Clair River. In 1982, caged clams were exposed at 13 sites extending from Sarnia to the St. Clair River delta as described by Kauss and Hamdy (1985). In 1984, clams were exposed at 17 sites chosen to delineate source areas better. The soft tissue of the clams were analysed for HCB, OCS, pentachlorobenzene (QCB) HCBd, 2,4,6-trichlorotoluene (TCT), PCB, aldrin, DDT, chlordane, p,p'-DDE, p,p'-DDD and α -BHC.

Organochlorines such as hexachlorobenzene, pentachlorobenzene, octachlorostyrene, hexachlorobutadiene and PCBs were accumulated to a significant degree by the caged clams. The extent of the bioaccumulation of these contaminants by the clam tissues was evident from detectable levels found in clams exposed at Port Lambton (Fig. 3.70a and b).

Although 1,2,4- and 1,3,5-trichlorobenzene and 1,2,3,5- and 1,2,4,5-tetrachlorobenzene were present in the ambient river waters, they were not accumulated to detectable levels by clam tissues. It is possible that these four compounds were more rapidly metabolized and eliminated by clams under the prevalent river flow and temperature conditions.

The major input area of the above compounds is the 1.8-km section of river front from the Township ditch to the Dow's 1st Street sewer complex. Additional inputs of these compounds, but at lower levels, also occurred in 1 km section from the mouth of Talford Creek (Shell Canada) to the bottom end of Petrosar.

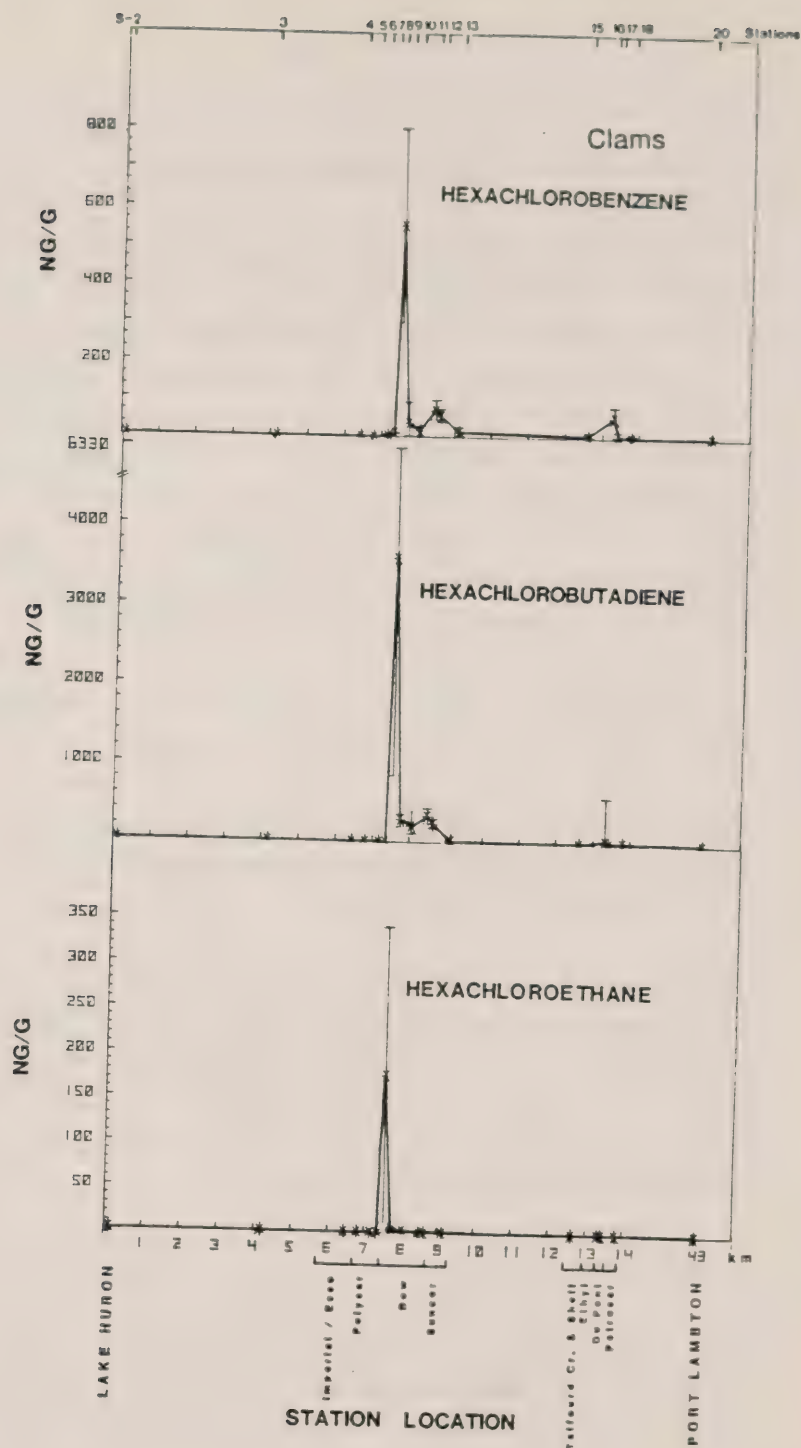


Figure 3.70a 1984 St. Clair River chlorinated organic compounds in clams.

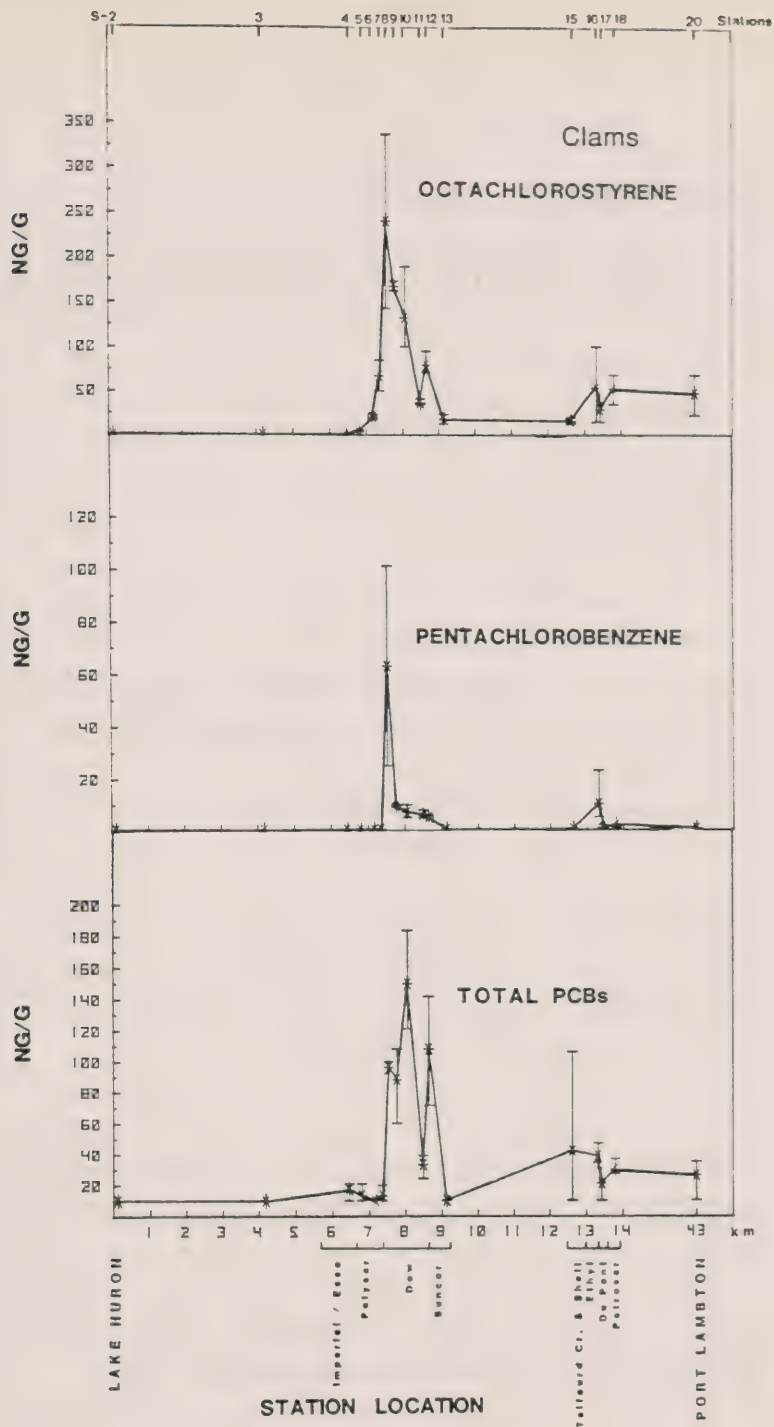


Figure 3.70b 1984 St. Clair River chlorinated organic compounds in clams.

AMBIENT CONDITIONS - CONCLUSIONS

Monitoring programs initiated by DOE and MOE during the period September to December 1985 indicated that ambient conditions (water, sediment and biota) are adversely affected by discharges from industries located in the Sarnia area, namely the chemical valley. This adverse impact was compounded by the effects of the August 13-16 spill of perchloroethylene from Dow's 1st Street sewer complex.

The contaminated puddle composition was mainly perchloroethylene during the September survey. In December, the puddle composition was perchloroethylene and carbon tetrachloride. The minor components of the puddles constituted HCB, HCB₂D, OCS, QCB, tetrachlorobenzene, hexachloroethane, trichlorobenzene, trichloroethylene and trichloroethane, comprising 3% of the total. These puddles were mainly found in an area 50 m square opposite the 1st Street sewer complex. The nature of the river bottom in the area where a trench exists resulted in accumulation of the puddles on the river bottom sediment. Dibenzo dioxins and dibenzo furans were found in the contaminated puddles but there was not 2,3,7,8-TCDD or 2,3,7,8-TCDF.

Chlorinated organics, such as hexachlorobenzene, hexachlorobutadiene, OCS, pentachlorobenzene, tetrachlorobenzene, trichlorobenzene, carbon tetrachloride and perchloroethylene, are found in water, sediment and biota along the Ontario shoreline of the river. The extent of impact was observed as far as the river mouth. There was little transboundary pollution observed from Ontario sources to the Michigan side of the river.

The compounds HCB, HCB₂D, OCB and 1,2,4-trichlorobenzene found in the ambient river water resulted in violations of the MOE and U.S. EPA criteria for the protection of aquatic life in certain sections of the river.

Although there were indications of definite presence of 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, pentachlorobenzene, benzene and carbon tetrachloride in the treated drinking water, there were no violations of the drinking water criteria at the downstream water supplies (Walpole and Wallaceburg).

During the course of the present study, sediment core samples indicated that the deeper layer (> 3 cm) is characterized by tarry material which may reflect the effect of previous discharges or spills. The identity and origin of this material are not known at present.

Surficial sediment results revealed that there were two areas with severe contamination with HCB, HCB₂D, OCB and OCS which are major by-products of the production of chlorine and chlorinated solvents manufactured by Dow Chemical. These areas were near the Township ditch which drains the Dow Scott Road landfill site, and in the vicinity of the Dow 1st Street sewer complex. The most significant of these two sources appeared to be Dow's 1st Street sewers. This contamination is a consequence of perchloroethylene liquid losses in conjunction with continuous discharges of the chlorinated organics. Traces of dibenzodioxins and furans were found but no 2,3,7,8-TCDD or TCDF were detected. It appears that these two areas have a localized effect on the river bottom dwelling organisms. There was a general improvement in the health of the benthic community during

the period 1977-1985, with the exception of a section of approximately 100m long along Dow's shoreline where forms of life were absent. The perchloroethylene spill has contributed to this impairment. Also, sediment in this section was acutely toxic. Effects of industrial discharges on the higher food chain (e.g., sport fish) were detected. However, contaminants such as HCB, PCBs, OCS and mercury have declined in sport fish (edible portion) significantly in the last decade.

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APPENDIX

Chemicals listed are of environmental significance and have been identified in various aquatic compartments of the St. Clair River. The Ministry of Environment (MOE) Provincial Water Quality Objectives (PWQO) are designed to protect aquatic life. Where possible, other water quality criteria have been listed. Fish consumption guidelines for mercury and PCB's have been developed by Health & Welfare Canada and adopted for use in Ontario. Aquatic compartments, where chemicals have been identified, include water (W), sediment (S), biota (B) and industrial effluent (E).

The environmental significance of a chemical is indicated in terms of its environmental persistence, toxicity to aquatic biota and potential for bioaccumulation. Also, included in this section of the table is information on the carcinogenic properties of various chemicals.

A carcinogen is a chemical that has produced positive carcinogenic results in more than one replicated animal laboratory test but may or may not have been confirmed epidemiologically or clinically in human studies. A possible carcinogen is a chemical that has been shown carcinogenic in at least one animal study. A mutagen has been shown to be mutagenic in more than one replicated short-term bioassay. A teratogen is a chemical that has produced significant reproductive effects in animal studies.

Environmental persistence has been assessed according to the following categories ($t_{1/2}$ = half-life).

<u>Category</u>	<u>$t_{1/2}$ in weeks in water or sediment</u>
Very Persistent	> 52
Persistent	40-52
Non-Persistent	< 40

Toxicity to aquatic biota has been assessed according to the following categories.

<u>Aquatic Toxicity Category</u>	<u>96 hr. LC₅₀ (mg/L)</u>
Extremely toxic	< 1
Highly toxic	1-10
Moderately toxic	10-100
Slightly toxic	100-1000
Relatively non-toxic	> 1000

Bioaccumulation potential has been assessed according to the following categories:

<u>Bioaccumulation Category</u>	<u>Bioaccumulation Factor</u>
Extreme	> 100,000
High	10,000-100,000
Moderate	1,000-10,000
Low	100-1,000
Non	< 100

CONTAMINANTS OF POTENTIAL CONCERN - ENVIRONMENTAL SIGNIFICANCE AND OBJECTIVES

CHEMICAL NAME	MOE FWQO	OTHER AMBIENT WATER QUALITY OBJECTIVES	FISH CONSUMP.	AQUATIC COMPART.	ENVIRONMENTAL SIGNIFICANCE
1,1,1-TRICHLOROETHANE					
1,1,2,2-TETRACHLOROETHANE				WE	mod. toxic, non-persistent, mutagen
1,1,2-TRICHLOROETHANE				WE	mod. toxic, non-persistent, carcinogen
1,1,2-DICHLOROETHYLENE				W	mod. toxic, non-persistent, carcinogen
1,2,3,5-TETRACHLOROBENZENE	0.10 µg/L			WE	slightly toxic, non-persistent, possible carcinogen
1,2,4,5-TETRACHLOROBENZENE	0.15 µg/L			WE	extreme. toxic, mod. persistent, mod. bioaccumulation
1,2,4-TRICHLOROBENZENE	0.05 µg/L			WE	extreme. toxic, mod. persistent, mod. bioaccumulation
1,2-DICHLOROBENZENE	2.5 µg/L			SE	mod. toxic, mod. bioaccumulation
1,2-DICHLOROETHANE				SEB	highly toxic, low bioaccumulation, carcinogen tests inconclusive
1,2-DICHLOROPROPANE				WE	slightly toxic, non-persistent, carcinogen
1,2-DICHLOROPROPENE	2.5 µg/L			E	mod. toxic, mutagen
1,3-DICHLOROBENZENE	4.0 µg/L			SEB	highly toxic, low bioaccumulation
1,4-DICHLOROBENZENE				SEB	extreme. toxic, low bioaccumulation, carcinogen tests inconclusive
2,3,7,8-TCDD		non-detectable (AEOC)	20 ng/kg B	SEB	persistent, very toxic
2,4,5-TRICHLOROPHENOL	18 µg/L			E	extreme. toxic, non-persistent, possible carcinogen
2,4,6-TRICHLOROPHENOL	18 µg/L			E	extreme. toxic, non-persistent
2,4-DINITROTOLUENE				E	mod. toxic, mutagen
ANTHRACENE				S	mod. toxic, low bioaccumulation
BENZENE	25 µg/L*			WE	mod. toxic, low bioaccumulation, non-persistent, carcinogen
BENZO(A)ANTHRACENE				S	carcinogen
BENZO(A)PYRENE				S	mod. bioaccumulates, mod. persistent, carcinogen
BENZO(B)FLUORANTHENE		0.01 µg/L & 1 µg/g (AEOC)		S	carcinogen
BENZO(K)FLUORANTHENE				S	carcinogen
BIS(2-ETHYHEXYL)PHTHALATE	0.6 µg/L			S	highly toxic, mutagen, teratogen
CADMIUM	0.2 µg/L	0.7 µg/L (see USEPA)		SB	extreme. toxic, mod. bioaccumulates
CAL-SOMETRACHLORIDE				WE	slightly toxic, non-persistent, carcinogen
CHLOROBENZENE	15 µg/L			E	mod. toxic, low bioaccumulation
CHLOROFORM				WE	slightly toxic, non-persistent, carcinogen
DIELDRIN	0.001 µg/L			S	extreme. toxic, persistent, carcinogen
ETHYLBENZENE	700 µg/L*			E	mod. toxic, non-persistent
FLUORANTHENE				S	mod. bioaccumulation
HEXACHLOROBENZENE	0.0065 µg/L			SB	extreme. toxic, high bioaccumulation, very persistent, mutagen
HEXACHLOROBUTADIENE				SB	extreme. toxic, carcinogen
HEXACHLOROBUTENE				S	

CONTAMINANTS OF POTENTIAL CONCERN - ENVIRONMENTAL SIGNIFICANCE AND OBJECTIVES (con't.)

CHEMICAL NAME	MOE PWQO	OTHER AMBIENT WATER QUALITY OBJECTIVES	FISH CONSUMP.	AQUATIC COMPART	ENVIRONMENTAL SIGNIFICANCE
HEXACHLOROETHANE				SE	
HEXACHLOROPROPANE				S	mod. toxic
LEAD	25 µg/L	2.8 µg/L (see USEPA)		B	extreme. toxic
MERCURY	0.2 µg/L	0.012 µg/L (USEPA)	0.5 µg/g SB	SB	extreme. toxic, highly bioaccumulative
OCTACHLOROSTYRENE				WSBE	
OIL AND GREASE				S	indicator of organic chemical contamination
PCBs	0.00 µg/L		2.0 µg/g SB	SB	high bioaccumulation, very persistent
PCDDs					toxicity, bioaccumulation and persistence vary with chlorine substituents
PCDFs					toxicity, bioaccumulation and persistence vary with chlorine substituents
PENTACHLOROBENZENE	0.03 µg/L			WSBE	extreme. toxic, high bioaccumulation
PENTACHLOROBUTADIENE				S	
PENTACHLOROETHANE				S	mod. toxic
PENTACHLOROCYCLOPROPANE					
PENTACHLOROPHENOL	0.5 µg/L	0.4 µg/L (AEOC)		E	extreme. toxic, very persistent
PENTACHLOROPROPANE				S	
PENTACHLOROPROPENE				S	
PERCHLOROETHYLENE				WE	mod. toxic, non-persistent, carcinogen
PERYLENE				S	
PHENANTHRENE				SB	low toxic
PYRENE				SB	extreme. toxic
STYRENE	100 µg/L*			E	mod. toxic, non-persistent
TETRACHLOROBUTANE				S	
TOLUENE	250 µg/L*			E	mod. toxic, non-persistent
TRICHLOROETHYLENE				WE	mod. toxic, non-persistent, mutagen, possible carcinogen
TRICHLOROMETHANES				WE	non-persistent group of chemicals formed during chlorination

* MOE Interim Water Quality Guidelines

- these are objectives that have been scientifically set but have not been through a formal peer review and subsequent approval

USEPA United States Environmental Protection Agency

- for CADMIUM and LEAD these water quality criteria represent four-day average concentrations calculated specifically for the St. Clair River

AEOC Aquatic Ecosystem Objectives Committee

- the AEOC recommends the adoption of these objectives into the 1978 Great Lakes Water Quality Agreement, to be used, where applicable, together with existing objectives
The AEOC 1 µg/g objective for BENZO (A) PYRENE represents a recommended ambient sediment concentration

4. POINT SOURCE SURVEY AND URBAN RUNOFF

Introduction

The Ontario Region of the Environmental Protection Service, in co-operation with the Ontario Ministry of the Environment carried out a point source effluent screening survey for all major industries and municipal sources between and including Esso Petroleum and Suncor at the end of November 1985 (Table 4.1).

A list of facilities, sampling sites and the type of sample collected is contained in Table 4.1. Industrial intakes and process effluents and/or final effluent discharges to the St. Clair River were sampled. Intakes were analysed to determine the background contamination in water being used by the plants. The final effluent from the Sarnia municipal sewage treatment plant was also included.

In addition to the industrial/municipal point sources, a survey of the Township ditch, the Scott Road Outfall and the Dow Scott Road landfill was also conducted. The Township ditch discharge to the St. Clair River has historically been a source of contaminants. The Hydraulics Division of the National Water Research Institute (NWRI) also sampled the Sarnia municipal treatment plant, the Township ditch and urban storm sewers as part of its study on urban runoff. This information is also reported in this section.

A total of 24 water samples were collected. A single sediment sample from the Township ditch was also collected. Liquid samples were analysed for volatile organics, chlorobenzenes and other chlorinated extractable compounds, polynuclear aromatics

(PAHs) and chlorophenols. The sediment sample was not amenable to volatiles analysis; however, chlorinated dioxins were analysed. Volatile organics were analysed by Barringer Magenta of Rexdale, Ontario. Chlorinated extractable organics, PAHs and dioxins were analysed by the National Water Research Institute (NWRI), Burlington, Ontario.

Appendix I (Tables 4.1 to 4.24) contains the analytical data. Appendix II provides brief descriptions of each of the sources sampled, including products and waste water treatment for the industries. Sampling methods and references for the analytical methods are contained in Appendix III. These appendices appear at the end of this chapter.

Three areas of discussion follow. The first involves the matching of effluent composition with the contaminants present in the perchloroethylene puddles found on the river bottom, offshore of Dow Chemical. The effluent characteristics of some of the Dow sewers suggest that a continuing input of many of the contaminants in the perchloroethylene puddles is occurring. The second area of discussion highlights the overall findings of the industrial effluent survey and attempts to identify potential areas of concern. A comparison with the last major effluent survey data of 1979/80 is also made.* Lastly, the contamination of the Township Ditch by the Scott Road landfill and other sources is reviewed.

* St. Clair River Point Source Survey 1979-80, MOE/EPS 1985.

ST. CLAIR RIVER STUDY AREA

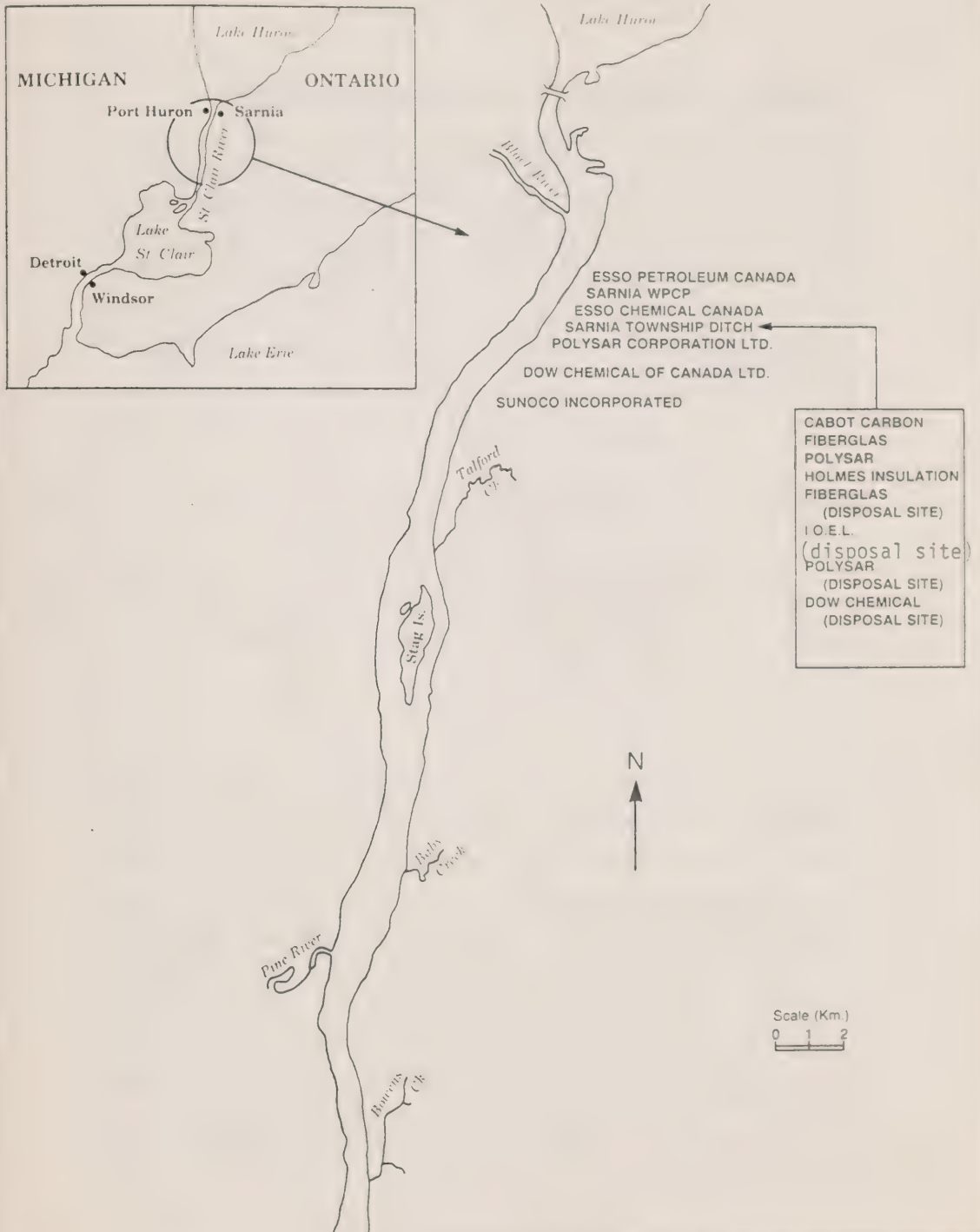


Figure 4-1

Comparison of Effluents with Perchloroethylene Puddles

The chemical composition of the perchloroethylene puddles discussed in the Perchloroethylene Puddles section of the report can be compared with the characteristics of the effluent samples collected during the study. The major components of the puddles were 60% perchloroethylene (tetrachloroethylene) and 30% carbon tetrachloride. Additional minor components (about 3%) which were also quantified are:

Hexachloroethane	0.8%
Hexachlorobutadiene	0.6%
Hexachlorobenzene	0.4%
1,1,1-trichloroethane	0.5%
Trichloroethylene	0.3%
Octachlorostyrene	0.02%
Pentachlorobenzene	0.01%
Tetrachlorobenzenes	0.02%
Trichlorobenzenes	0.02%

All of the above compounds were analysed in point source effluents as well as the Scott Road/Township ditch samples. Table 2 compares the relative magnitude of concentrations for each of the above parameters in the Dow point source effluents (concentrations for the 11 components were totalled and percentages based on the total were calculated; total was multiplied by 1.07 since the 11 compounds represent approximately 93% of the river bed material). None of the other point source effluents were significant sources of perchloroethylene or carbon tetrachloride, the major components of the perchloroethylene puddles, and are therefore excluded (see Volatile Organics Tables 4.3 to 4.8).

The percentage results do not match exactly, though perchloroethylene and carbon tetrachloride are the major components in many cases (25 to 51% and 30 to 95% respectively). The 1st Street sewers appear to be the major sources of many of the 11 contaminants suggesting that there is a continuing input. Perchloroethylene and carbon tetrachloride are the major parameters in the 1st Street 42" sewer and the 30" Acid Tile especially. Elevated concentrations of these pollutants were also found in samples of the Dow effluents collected by MOE, September 23 to 27, 1985 (Table 4.21).

In conclusion, the Dow Chemical sewers are a continuing source of the major components found in the perchloroethylene puddles, while the other sources surveyed are not. The total daily loadings of perchloroethylene and carbon tetrachloride from the Dow sewers were approximately 14 kg/d and 26 kg/d respectively.

In terms of the minor components of the perchloroethylene puddles such as hexachloroethane, hexachlorobutadiene, hexachlorobenzene and other chlorinated benzenes and chloroethanes (Tables 4.9 to 4.12), Dow, including the Dow Scott Road landfill, is again the major source though traces of these compounds (up to 0.20 ug/L) were found in the Suncor, Esso Petroleum, Sarnia WPCP, Polysar and Esso Chemicals effluents.

Overall Findings

The St. Clair Study allows a characterization of the effluents, keeping in mind that only a single sample was collected. The variability of the discharges cannot be assessed. However, the chemical characteristics of the sources sampled can be determined. Each source is discussed below in these terms. New York State (NYS) ambient water quality standards and guidelines were consulted to determine the significance of some of the trace data (Table 4.22). These criteria are intended to protect human health in terms of drinking water supplies and contact recreation and should be met at the edge of the mixing zone. In addition, the U.S. EPA proposed organic chemicals industry effluent limitations guidelines were also used to interpret the data. Best Available Technology (BAT) Option I effluent limits were used. These are expected to be met with existing Best Practicable Technology (BPT). If a BAT I effluent guideline was not available for a given contaminant, BAT Option II values were used. These limits are meant to be met using Best Available Technology.

1. Esso Petroleum

Treated process effluent from the Esso refinery was sampled. This effluent mixes with cooling water prior to discharging to the river. This effluent was not a source of volatile organics (Table 4.3). Low concentrations of chlorinated extractables and chlorophenols, all below NYS ambient water quality criteria were detected in the effluents. The Biox

effluent contained many of the PAHs analysed at low concentrations with acenaphthylene only exceeding 1 ug/L.

2. Esso Chemical

The major volatile in the Esso Chemical final effluent was vinyl chloride at 66 ug/L (Table 4.3) which is just over the U.S. EPA Option II BAT daily maximum effluent limit. This is equivalent to a loading of 2.3 kg/d. Like the Esso Petroleum Biox effluent, this discharge contained very low concentrations of chlorinated extractable compounds. A pattern of PAHs at low concentrations similar to the refinery effluent was also present, acenaphthylene being the only component in excess of 1 μ g/L.

3. Sarnia WPCP

The sewage treatment plant effluent contained low concentrations of volatile organics including perchloroethylene at 3.7 ug/L (EPS sample - Table 4.3) and at 26 ug/L (NWRI sample). Extractable chlorinated organic compounds were present at very low concentrations below NYS ambient water quality standards and guidelines (Tables 4.9, 4.13 and

4.23). PAHs were also present at low concentrations (Table 4.17).

4. Polysar Limited

With the exception of benzene, the concentrations of volatiles in the Polysar effluents were quite low. Polysar is a major source of benzene (Table 4.4), originating mainly with the 72" sewer (4,000 ug/L or 110 kg/d). The U.S. EPA BAT Option I daily maximum for this compound is 245 ug/L. The Polysar effluents contained very low concentrations of chlorinated extractable compounds, many of which appear to originate with the intake (Tables 4.10 and 4.14). Very low concentrations of PAHs were present in the effluents (Table 4.18).

RECOMMENDATION

The source of benzene in the Polysar 72" sewer should be identified and treated.

5. Dow Chemical

The Dow sewers contained a broad range of volatiles at elevated levels compared with the other point sources (Table 4.5). The 1st Street 48", 2nd Street and 4th Street sewers were the least contaminated. The most significant

volatile organics in the remaining sewers (i.e., in excess of 100 ug/L) were:

1st Street 42" Sewer:	1,2-dichloroethane*
	Perchloroethylene
1st Street 30" Acid Tile:	1,1-dichloroethene *
	1,1-dichloroethane
	1,2-dichloroethane*
	1,1,1-trichloroethane*
	Carbon Tetrachloride
	Trichloroethene*
	1,1,2-trichloroethane*
	Perchloroethylene*
1st Street 54" Sluice:	1,2-dichloropropane
3rd Street Sewer:	Benzene*
	Ethyl benzene*
	Styrene

The total loading of U.S. EPA volatile priority pollutants from Dow was estimated to be 242 kg/d (Table 4.8). U.S. EPA has not developed an effluent limit for styrene.

Compared with the other point sources sampled, Dow was the major source of neutral extractable chlorinated organics, especially 1,2,4-trichlorobenzene, hexachlorobenzene, hexachloroethane and hexachlorobutadiene (Table 4.11).

* Compounds present in the effluents in excess of U.S. EPA BAT OPTION I or II daily maximum effluent concentrations.

The 1st Street 42" sewer and 30" Acid Tile were the main sources of these compounds. 1,2,4-trichlorobenzene was discharged below the New York State ambient water quality standard for the sum of all trichlorobenzenes of 10 ug/L. The remaining compounds generally require a 1 in 200 dilution to meet the New York ambient water quality standards and guidelines.

The Dow sewers contained very low concentrations of chlorophenols, three of which may have originated with the intake water (Table 4.15). Dow appears to be a minor source of polynuclear aromatics.

RECOMMENDATIONS

1. *The effluent levels of volatile organics, particularly perchloroethylene and carbon tetrachloride, should be reduced.*
2. *Based on the findings for water and sediments, the effluent levels of persistent chlorinated organics, notably hexachlorobutadiene and hexachlorobenzene should be reduced.*
3. *The source of ethylbenzene and benzene in the Dow 3rd Street sewer should be identified and treated.*

6. Suncor

Compared with the other refinery samples, the Suncor impounding basin effluent was more contaminated. However, the Suncor intake, located downstream of Dow Chemical, was the most contaminated of those sampled. Many of the contaminants being discharged by Dow and Polysar (benzene only) were detected in the intake. This includes carbon tetrachloride (3.5 µg/L), perchloroethylene (5.6 µg/L), benzene (23 µg/L) and chlorinated extractable compounds.

On the day of sampling, the refinery experienced a major power failure which resulted in an emergency shutdown of part of the operation and a fire in one unit area. This may have placed an extra load on the wastewater treatment plant so that the data may not reflect normal conditions.

Suncor's wastewater treatment system is presently being expanded so that all wastewater from the refinery will be biologically treated (on line late 1986).

The impounding basin effluent contained slightly elevated concentrations of 1,2-dichloroethane, 1,1,1-trichloroethane, benzene and xylenes (Table 4.3). Very low concentrations of neutral extractable chlorinated compounds and essentially no chlorophenols were present. All of the PAHs analysed were found including naphthalene at 23 µg/L, fluorene at 1.9 µg/L and phenanthrene at 2.3 µg/L.

Comparison with 1979/80 Survey Data

The results for the six week survey were compared with historical data gathered in 1979 and 1980 (St. Clair River Point Source Survey 1979/80, MOE/EPS September 1985). It should be noted that the 1979/80 study involved more extensive sampling (3 to 8 days) as compared with the present study (1 day). In the 1979/80 report, the data was presented in ranges such as 10 to 100 µg/L. The results of this comparison are summarized for each facility and the Township ditch below.

1. Esso Petroleum

Three compounds found in the 10 to 100 µg/L range in 1979/80 were all below 1 µg/L in the present survey (chloroform, fluorene, hexachlorobenzene).

2) Esso Chemical

Nine compounds found in the 10 to 100 µg/L range in 1979/80 were all below 1 µg/L in the present survey (methylene chloride, benzene, toluene, naphthalene, acenaphthylene, acenaphthene, fluorene phenanthrene and pentachlorophenol).

3) Polysar

Six compounds found in the 10 to 100 µg/L range in 1979/80 were below 3 µg/L in the present survey. Benzene, present at 4,000 µg/L in the 72" sewer in 1985 had not been seen

previously. The Stereo API has historically contained high concentrations of benzene (1 to 10 ug/L to 10,000 to 100,000 ug/L in 1979/80, 500 ug/L 1985).

4) Dow Chemical

The Dow 2nd and 4th Street sewers were not sampled in 1979/80. The remaining outfalls are discussed individually below.

i) 1st Street 42" Sewer

In both 1979/80 and 1985, the following compounds were found in the 10 to 100 ug/L range or greater: Chloroform, 1,2-dichloroethane, carbon tetrachloride, 1,1,2-trichloroethane, perchloroethylene or 1,1,2,2-tetrachloroethane (one in four samples 1979/80).

The following compounds were found in the 10 to 100 ug/L or greater range in 1979/80 but below 5.6 ug/L in the present study: methylene chloride, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,2-dichloropropane, benzene, bromoform.

ii) 1st Street 48" Sewer

Seven compounds found in the 10 to 100 ug/L range in 1979/80 were found below 3 ug/L in the present study (1,1-dichloroethane, 1,2-dichloroethane, carbon tetrachloride, 1,2-dichloropropane, benzene, bromoform and perchloroethylene).

iii) 30" Acid Tile

In both 1979/80 and 1985, the following compounds were found in excess of 100 ug/L: 1,1-dichloroethane, 1,2-dichloroethane, carbon tetrachloride, trichloroethene, 1,1,2-trichloroethane and perchloroethylene.

The following compounds were present in excess of 10 ug/L 1979/80 and 1985: Methylene chloride, 1,1-dichloroethene (530 ug/L 1985), chloroform (100 to 1,000 ug/L 1979/80 one sample of three), 1,1,1-trichloroethane (710 ug/L 1985) and 1,2-dichloropropane.

The following compounds were present in excess of 10 to 100 ug/L or greater in 1979/80, but not in the present survey: Bis (2-chloromethyl) ether, benzene, toluene, ethylbenzene, hexachlorobutadiene and naphthalene.

iv) 54" Sluice

Three compounds were present in the 1979/80 and 1985 data in the 10 to 100 ug/L range: 1,2-dichloroethane, 1,2-dichloropropane, perchloroethylene. Carbon tetrachloride and 1,1,1-trichloroethane were in this range in the recent survey.

v) 3rd Street Sewer

In the 1979/80 samples, carbon tetrachloride and benzene were found in the 10 to 100 ug/L range in one of three samples. The 1985 sample contained 95 ug/L of carbon

tetrachloride and 490 µg/L of benzene as well as high concentrations of ethylbenzene (500 µg/L) and styrene (not measured in 1979/80).

5) Suncor

The following compounds were found in 1979/80 in the range of 10 to 100 µg/L or greater, but not in the present survey: methylene chloride, chloroform, trans-1,3-dichloropropylene, perchloroethylene, acenaphthylene, fluorene, phenanthrene, fluoranthene, pyrene, benzo (a) anthracene, 2,4-dichlorophenol and 2,4,6-trichlorophenol.

The concentrations of benzene and 1,2-dichloroethane were in the effluent in excess of 10 µg/L in 1985 only.

6) Township Ditch Before Polysar

Compounds present in the 1979/80 ditch samples in the 10 to 100 µg/L range were benzene and bromoform. In the present study chloroform and 1,2-dichloroethane were in this range.

7) Intakes

Intakes were sampled in both 1979/80 and the present survey. Of the 33 compounds identified in 24 samples at 8 intakes in 1979/80, 6 were identified at levels greater than 10 µg/L on 14 occasions in 1979 (1,2-dichloroethylene, chloroform,

trans-1,2-dichloroethylene, 1,2-dichloropropane, di-n-butylphthalate (not analysed 1985) and bis (2-ethyl hexyl) phthalate (not analysed 1985). Other intakes contained trace contaminants generally below 1 ug/L. The Suncor intake contained benzene (23 ug/L), perchloroethylene (5.6 ug/L) and carbon tetrachloride (3.5 ug/L) all of which were present at elevated concentrations in the Dow sewers and Polysar's 72" sewer (benzene only). Overall, intake water quality was improved compared with 1979.

Dow Scott Road Landfill, Scott Road Outfall and Township Ditch

During the Point Source Survey samples of the Dow Scott Road landfill before and after carbon treatment were collected to assess the efficiency of treatment and to determine the landfill's contribution to the Scott Road ditch. The Scott Road ditch outfall to the Township ditch and the Township ditch itself, upstream of Polysar at the ArmaK Chemicals Building west of Vidal Street, were also sampled (see Fig. 4.2). NWRI also sampled the Scott Road outfall and the Township ditch just before it passes west under Vidal Street, i.e., upstream of the EPS sampling site.

The Dow Scott Road landfill has a collection system for leachate and surface runoff which collects in a lagoon on the north side of the site. An interlocking sheet-steel dike completely surrounds the site and extends 5 m below ground into heavy clay. The lagoon contains high concentrations of volatile organics with 1,2-dichloroethane, carbon tetrachloride, 1,1,2-trichloroethane, and perchloroethylene greater than or equal to 1,000 ug/L (Table 4.6). Elevated concentrations of neutral

extractable organics are also present including hexachloroethane, hexachlorobutadiene and 1,4-dichlorobenzene. Chlorophenols such as 2,4,5-trichlorophenol and 2,4-dichlorophenol were present as well as the herbicides 2,4-D and 2,4,5-T (Table 4.16), suggesting that 2,4-D waste may have been disposed of at the site. PAHs (Table 4.20) are present at low concentration, with naphthalene being slightly elevated (4.7 µg/L).

The effectiveness of carbon treatment is difficult to interpret for some of the volatile compounds which actually appeared to increase in concentration, perhaps due to the saturation of the carbon and/or analytical variability. Others were decreased or eliminated (below detection limit). Carbon treatment was more consistent for the chlorinated extractables which were consistently reduced (Table 4.12). Hexachlorobutadiene and 1,2,4-trichlorobenzene remained in the landfill discharge above 1 µg/L. Chlorophenols were reduced below their detection limits, however, there was little effect on the chlorophenoxy acids (2,4-D, 2,4,5-T). PAHs were also reduced.

RECOMMENDATION

The effectiveness of the Dow Scott Road landfill carbon treatment facility should be investigated. Modifications should be implemented to reduce losses of persistent chlorinated organics, especially hexachlorobenzene and hexachlorobutadiene.

The Scott Road outfall drains the east side of Scott Road south to Hwy 40B and discharges into the Township ditch. It receives cooling water from Holmes Insulation, surface runoff,

SARNIA TOWNSHIP DITCH

HWY 40 B

HOLMES INSULATION
COOLING WATER

IMPERIAL OIL DISPOSAL SITE
RUNOFF

IMPERIAL AVE.

POLYSAR DISPOSAL SITE

FIBERGLASS DISPOSAL SITE

DOW DISPOSAL SITE

CITY OF SARNIA
SLUDGE LAGOONS

SCOTT RD.
DITCH AND
TILE DRAIN

FIBERGLASS
FACTORY

CABOT
CARBON

POLYSAR

TREATED
PROCESS
AND
COOLING

SUPERNATANT
TO WPCP
FOR TREATMENT

DOME
PETROLEUM

IMPERIAL OIL
TANK FARM
RUNOFF*

ESSO
CHEMICAL
STORM
WATER

TREATED
PROCESS
AND
COOLING

CONDENSATE, STORM
WATER & COOLING

R&D

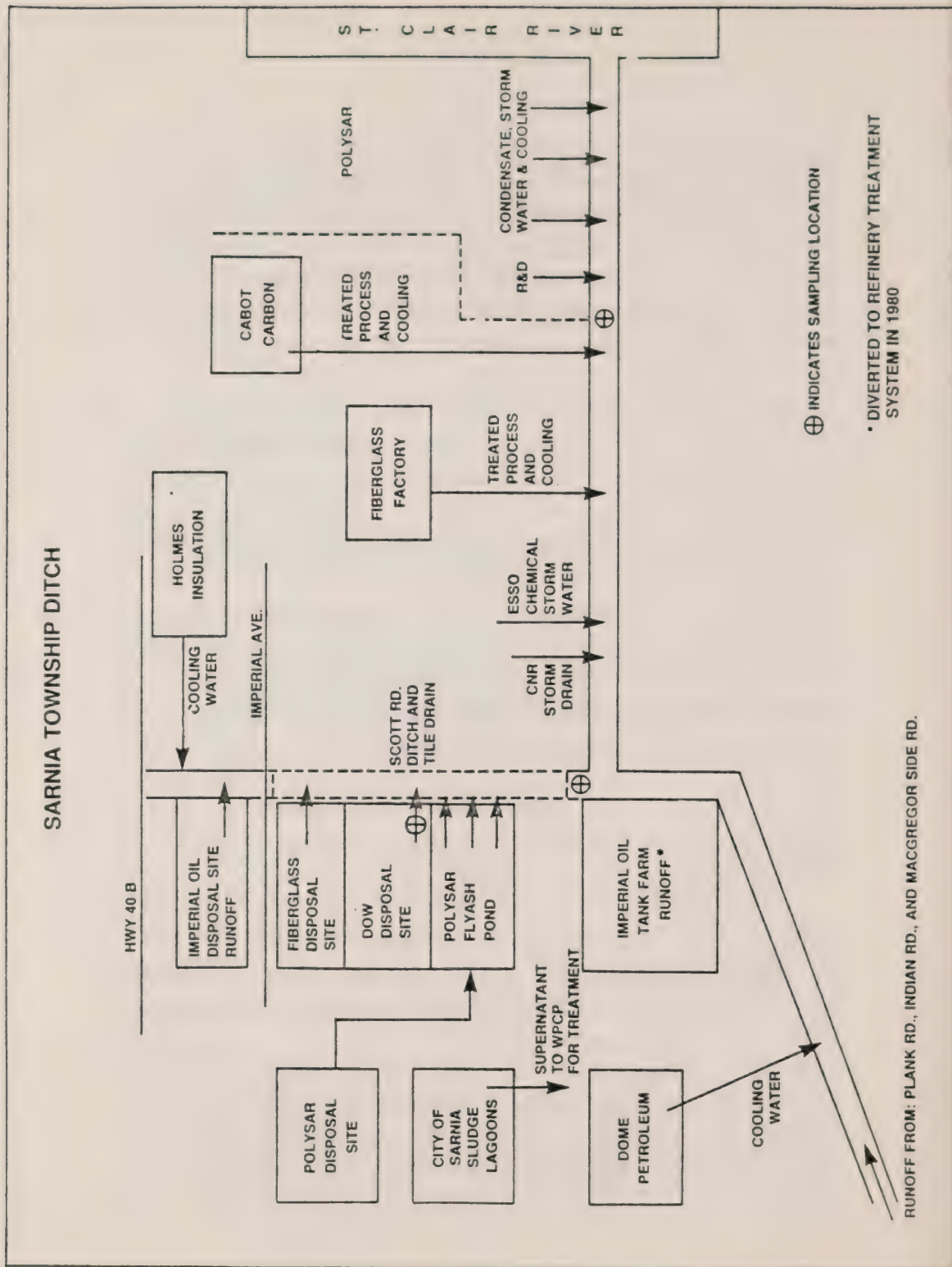
COOLING
WATER

⊕ INDICATES SAMPLING LOCATION

* DIVERTED TO REFINERY TREATMENT
SYSTEM IN 1980

RUNOFF FROM: PLANK RD., INDIAN RD., AND MACGREGOR SIDE RD.

S T C L A I R R I V E R



Dow landfill effluent and periodic discharges from the Polysar and Fiberglass landfills. The volatile organics detected were the same as those found in the Dow Scott Road discharge, though at lower concentrations; 1,2-dichloroethane (910 $\mu\text{g/L}$) and 1,1,2-trichloroethane were at the highest concentrations (Table 4.6). NWRI also identified perchloroethylene in this outfall and similar values for the chlorinated extractable compounds (Table 4.23).

Reduced levels of chlorinated organics were also encountered, however, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene were at higher concentrations in the Scott Road outfall than in the Dow Scott Road landfill, suggesting that there is an additional source of these compounds. Chlorophenols and 2,4-D/2,4,5-T remained at low concentrations.

RECOMMENDATION

Additional sources of chlorinated organics to the Scott Road outfall, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene in particular, should be investigated.

The Township ditch upstream of Polysar contained low concentrations of organics, though chloroform, 1,2-dichloroethane, 1,4-dichlorobenzene, 1,2,4-trichlorophenol and hexachlorobutadiene stand out. The ditch has the characteristics of an industrial effluent as opposed to surface runoff. The NWRI sample east of Vidal Street contained similar concentrations of perchloroethylene, hexachlorobutadiene and other compounds (Table 4.23).

Due to historical contamination of the Township ditch, principally originating with the Dow Scott Road landfill, a 3.7 km section of the ditch up to Polysar was excavated by Dow in 1983-84. No background data was available for the excavated sediments.

RECOMMENDATION

Sources of chlorinated organics to the Township ditch, in addition to the Scott Road outfall, should be investigated.

A sediment sample was collected from the bottom centre of the Township ditch at the bridge leading to the Armak Chemicals Building using an Ekman dredge. The sediment was mainly clay as opposed to silt or mud. The sample contained parts per million concentrations of dichlorobenzenes, 1,2,4-trichlorobenzene, hexachlorobenzene, hexachlorobutadiene and octachlorostyrene. Dioxins were also analysed. No tetra, penta or hexachloro dibenzo-p-dioxin were detected. Heptachlorodioxin was present at 0.17 ug/kg. Octachlorodioxin was also present (0.44 ug/kg).

RECOMMENDATION

The extent and degree of contamination of the Township ditch sediments should be further investigated.

Urban Runoff

Urban runoff is recognized as a non-point source of trace organics. Runoff is discharged into receiving waters via combined sewer overflows, storm water discharges, and overland flow.

A survey of the Point Edward/Sarnia area identified 12 outfalls which discharge runoff into the St. Clair River. These 12 outfalls comprise four combined sewer overflows and seven storm sewers. Additional outfalls drain the adjacent industrial area.

Recognizing the effects of land use on runoff quality, it was desirable to subdivide the developed area into two sub-areas and to design the sampling program accordingly. The first sub-area represents Point Edward and Sarnia (without the industrial part) and the second sub-area represents the chemical industry along Vidal Street South (Esso, Polysar, Dow).

The non-industrial sub-area comprises about 21 km² of primarily residential urban land. To estimate the loading of trace organics in runoff from this area, it was necessary to calculate the annual runoff volume and to estimate its composition by sampling. The annual runoff volume was estimated by the Soil Conservation Service (SCS) method* as $5.2 \times 10^6 \text{ m}^3/\text{year}$. An additional volume is discharged in the form of combined sewer overflows which are estimated as 5% of the annual sewage volume,

* A procedure developed by the U.S. SCS and widely used in Canada for computation of surface runoff on the basis of soil and surface classifications.

or $1.1 \times 10^6 \text{ m}^3/\text{year}$. Thus the total annual volume of runoff and overflows from this sub-area is $6.3 \times 10^6 \text{ m}^3/\text{year}$. Using mean concentrations of suspended solids in this volume, the annual yield of suspended solids was estimated as 1100 tonnes/year.

Samples of runoff and wet weather flows in combined sewers were collected at three sites listed in Table 4.23. The first site was a combined sewer overflow structure at Clifford Street. The second site was located on Campbell Street, just east of Whitmore Avenue. The third site was located on Cathcart Boulevard, east of Lecaron Avenue, quite far from the industrial area.

Analytical results for water samples collected at these three sites are given in Table 4.23 for the major components of the perchloroethylene puddles. The results do not show much variation. The lowest levels were found at the Clifford Street overflow which mainly drains an industrial area. Two-thirds of the data were below the detection limit.

The second sub-area was the industrial area at the sound end of the City of Sarnia. This sub-area comprises 4 km^2 of industrial land enclosed by the St. Clair River, St. Clair Parkway, Vidal Street South and Christina Street. Two sampling sites were established along the Vidal Street perimeter of the sub-area. The Vidal Street North site was established at the junction of Vidal and Andrew Streets. The Vidal Street South site was established about 100 m north of Churchill Road. Since the whole area is served by private roads and sewers, it was not possible to establish other sites closer to the sewer outfalls.

The analytical results obtained for both industrial sites are shown in Table 4.23. Although the contaminant levels observed were somewhat higher than those in residential areas, the differences were not pronounced.

The annual runoff from the industrial sub-area was estimated as $1.7 \times 10^6 \text{ m}^3/\text{year}$ and this volume is expected to carry about 700 tonnes of suspended solids.

Since the differences in the composition of residential and industrial runoff were relatively small, it was decided to combine both sub-areas in calculations of loadings. Thus, the combined area produces about $7.8 \times 10^6 \text{ m}^3/\text{year}$ of runoff and about 1800 tonnes/year of suspended solids. In annual loading calculations, the maximum runoff concentrations from Table 4.23 were adopted to compensate for non-monitored inputs within the industrial area. The calculated loadings are also given in Table 4.23. Considering that these loadings are annual as opposed to daily, the values for urban runoff are very low.

In conclusion, urban runoff is a very minor source of the components of the perchloroethylene puddles (Table 23) compared with industrial sources and the municipal water pollution control plant.

Besides water samples, a number of sediment samples were also collected. Analytical results given in Table 4.24 include data for both residential and industrial area sediment samples. The observed levels are relatively low except for the Township ditch. There was no need to consider these sediment data in loading calculations because of the extraction of unfiltered water samples when analysing liquid samples.

POINT SOURCE SURVEY CONCLUSIONS

1. Dow Chemical effluents, especially the 1st Street sewers, contain many of the same compounds as the perchloroethylene puddles found on the river bottom. The continuous discharge of contaminated effluents from the Dow 1st Street sewers does not in itself account for the formation of the perchloroethylene puddles.
2. Compared with the other point sources sampled, Dow was the major source of neutral extractable chlorinated organics, especially 1,2,4-trichlorobenzene, hexachlorobenzene, hexachloroethane and hexachlorobutadiene.
3. For the Esso Petroleum, Esso Chemical and Sarnia WPCP effluents, the contaminants analysed were generally found at very low concentrations requiring zero or minimal dilutions to achieve ambient water quality standards and objectives. The total net loadings of volatile hydrocarbons from these three sources were 0.96 kg/d, 2.6 kg/d and 2.0 kg/d, respectively.
4. Polysar was a major source of benzene originating mainly the 72" sewer. The total net loading of volatile hydrocarbons was 115 kg/d of which 112 kg/d was benzene.
5. The Dow sewers are significant sources of volatile pollutants compared with other industrial sources in the present survey and those studied previously on the Great Lakes. The total net loading for volatile hydrocarbons was estimated to be 242 kg/d. Six major pollutants accounted for 84% of this loading (1,2-dichloroethane, perchloroethylene, 1,2-dichloropropane, carbon tetrachloride, benzene and ethyl benzene). Ethylbenzene and benzene totalled 132 kg/d.

6. The Suncor intake, located downstream of Dow Chemicals, contains many of the compounds being discharged at high concentrations by Polysar (benzene only) and Dow. The total net loading of volatile priority pollutants from Suncor was 1.1 kg/d.
7. A comparison of historical organics data for 1979/80 with the present survey indicates some improvement, but a greater number of samples would be required to make a proper comparison coupled with an examination of abatement measures that have occurred during the period.
8. The Dow Scott Road Landfill leachate contains the chlorophenoxy herbicides 2,4-D (18 µg/L) and 2,4,5-T (1 µg/L), high concentrations of volatile organics including 1,1-dichloroethane, 1,2-dichloroethane, chloroform, trichloroethane and 1,1,2-trichloroethane. Loadings could not be calculated due to a lack of flow information.

The levels of 2,4-D and 2,4,5-T in the disposal site leachate appeared to be unaffected by carbon treatment. High concentrations of volatiles were also observed after carbon treatment. All chlorophenols were effectively removed by treatment. The Scott Road site was also a source of trichlorobenzene and hexachlorobutadiene. The Dow 1st Street 30" Acid Tile and the Polysar 66" Sewer also contained detectable levels of 2,4-D.

9. The Scott Road Outfall contains many of the contaminants discharged by the Dow Scott Road landfill, however, there may be other sources of chlorinated organics, especially chlorinated benzenes to the Scott Road ditch.

10. The Township ditch water at a point upstream of Polysar is moderately contaminated with volatile organics and extractable chlorinated compounds, specifically: chloroform, 1,2-dichloroethane, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene and hexachlorobutadiene. The loading of volatile hydrocarbons from the Township ditch was similar to that from Polysar. In terms of the loading of chlorinated extractable pollutants, the Township ditch was a greater source of hexachlorobutadiene and trichlorobenzenes than the Dow 1st Street sewers.
11. The Township ditch sediment collected upstream of Polysar is contaminated with chlorinated benzenes, hexachlorobutadiene, octachlorostyrene (found at low levels in most of the samples) and chlorophenols.
12. Urban runoff in the Sarnia area is a minor source of perchloroethylene, hexachloroethane, hexachlorobutadiene, pentachlorobenzene, hexachlorobenzene and octachlorostyrene.

Possible Underground Sources

Before it was ascertained that Dow Chemical was directly responsible for the perchloroethylene found on the bottom of the St. Clair River, the possibility was raised that a hydrogeological source of the contaminant existed. This was based on the fact that large quantities of industrial wastes were disposed of by deep well injection from 1958 to 1976 in the St. Clair River area. The St. Clair River Situation Report released by MOE and DOE on November 18, 1985, provides a description of these disposal practices.

MOE and DOE undertook a study on the CN Rail tunnel which provides an underground observation station to monitor the movement and quality of ground water. The tunnel, about 30 metres (100 feet) below the ground surface, crosses under the St. Clair River between Sarnia and Port Huron, Michigan. The tunnel was constructed in 1889-1890 and is approximately 1,830 metres (6,000 feet) in length. The tunnel was driven through the overburden between the river bed and the shale bedrock. The overburden consists primarily of silty clay till. Sand and gravel exist locally both above and below the tunnel elevation.

Ground water leakage into the tunnel is low (around 4,000 gpd) and occurs for the most part in a 160 m (520 feet) section on the Canadian side of the river. Leakage is directed to a sump and pumped out of the tunnel. Ground water samples were collected from the discharge sump and three piezometers in the tunnel on November 25, 1985. Detectable levels of chlorides, phenols, and polyaromatic hydrocarbons (PAHs) were found in the water samples from the piezometers (Table 4.25). Chlorinated hydrocarbons such as hexachlorobutadiene and octachlorostyrene

were found, at trace levels, in the discharge water sample (Tables 4.25 to 4.29 in Appendix I).

Phenols do not occur naturally in ground water. Measured levels greater than 10 parts per billion are indicative of contamination from industrial wastes. The results suggest that industrial wastes may be contaminating the ground water around the CN Tunnel on the Canadian side. A possible source could be wastes from the former disposal zone (Detroit River Group) that have percolated upwards. The path for liquid waste transport could include horizontal movement through the fresh water aquifer. The fresh water aquifer is found beneath the tunnel and above the Detroit River Group. The fresh water aquifer appeared to be contaminated locally in 1972 when several water wells began to discharge contaminated water. Pressures in the waste disposal zone have been high enough to produce a flow gradient upwards towards the fresh water aquifer. It is possible that contaminants have or are migrating towards the St. Clair River via the fresh water aquifer.

The pathways in the bedrock by which wastes may have reached the fresh water aquifer and the tunnel have not been positively identified but could be one or more of the following:

1. short circuiting up improperly plugged and abandoned oil, gas, salt and water wells in the vicinity;
2. migration through a regional network of natural fractures; and
3. upward movement along the annuli of the disposal wells or leakage through corroded parts of the well casings.

RECOMMENDATIONS

To ascertain whether the ground water flow pattern is as hypothesized, studies in the Sarnia area to determine the following are recommended:

- 1. The ground water flow pattern in the fresh water aquifer;*
- 2. The water quality in the fresh water aquifer and seepage discharge to the St. Clair River; and*
- 3. The hydraulic head relationships between the fresh water aquifer, the rock layers above the Detroit River Group, the deep well disposal zone and the caverns in the Salina formation.*

In addition to the short term study on the CN Rail Tunnel, MOE and DOE have initiated a number of studies on the potential contamination of the St. Clair River originating from waste sites and discontinued deep well disposal practices. These studies have been undertaken within a three year joint Canada-U.S. study of the Upper Great Lakes Connecting Channels. (This study is described extensively in the November 18, 1985, St. Clair River Situation Report.) The following is an abbreviated list of those studies:

- 1) Survey of waste sites and assembly of existing data; - the Geologic, hydrologic and hydrogeologic nature of waste disposal sites are being characterized. The potential transport of contaminants from these sites in surface water

and groundwater are being assessed. Hazardous waste sites will be ranked according to their potential adverse impact.

- 2) Specific investigations on Hazardous Waste Sites; - monitoring wells will be installed and water samples collected. Areas of groundwater discharge to the St. Clair River will be defined.
- 3) Assessment of Deep Well Disposal Practices; - new monitoring wells will be installed and existing potable/abandoned wells will be sampled in order to assess extent of contamination.
- 4) Assessment of Seepage of Groundwater into the St. Clair River; - the quantity and quality of seepage into the St. Clair River from the vicinity of historic deep-well disposal operations is being determined.

Present information and data indicate that the distribution of the fresh water aquifer is discontinuous and areas of contamination are likely localized within it. Consequently, more monitoring wells will be required. Continuing Ontario Ministry of the Environment programs will include fresh water aquifer sampling of the new monitoring wells and existing domestic wells.

Environment Canada is funding a project by the Great Lakes Institute of the University of Windsor to assess the quantity and quality of seepage from the bed of the St. Clair River in the vicinity of Sarnia. A final report is expected by March 1986.

SPILLS

There were 32 reported spill incidents from 1974 to date in which 10 or more metric tons of material were discharged to the St. Clair River.

In the 11 year period, 9 spills involving 1182 metric tons of oil products occurred of which a total of 91 metric tons was unrecovered. Four latex spills totalled 142 metric tons of which none was recovered. Eight inorganic material spills totalling 4720 metric tons, 4175 unrecovered, involved salts, acid, caustic and brine. Two spills of styrene involved 4915 metric tons, with 2780 metric tons unrecovered. The remaining seven spills of 559 metric tons, of which 393 metric tons was unrecovered, comprised phenolic wastewater (239 metric tons), perchloro-ethylene lignin liquor, ethylene glycol, process water, washwater and xylene.

In view of the frequency and potential significance of spills into the St. Clair River, the Ontario MOE is undertaking a critical review of spill control capabilities at each of the industries in the area. Improved 24-hour spill response has been provided by the recently established Spills Action Centre and enforcement activity has been strengthened by the addition of two investigation and enforcement officers to the Sarnia office.

SPILLS TO ST. CLAIR RIVER OR TRIBUTARIES
Involving 10 Tonnes or Greater of Material for Period 1974 to 1985

	Year	Source	Spilled (tonnes)	Est. Not Recovered* (tonnes)	Material
<u>Oil</u>	1976	Suncor	150	30	bunker C
	1976	Suncor	300	0	bunker C
	1977	CNR	86	17	bunker C
	1978	Esso Petroleum	29	0	gas oil
	1980	Hall Corp. (vessel)	21	13	bunker C
	1981	CNR	21	4	bunker C
	1981	Esso Petroleum	348	0	gasoline
	1984	Esso Petroleum	116	23	No. 2
	1984	Esso Petroleum	16	3	No. 2
	1985	Imperial Bedford (at Shell)	75	1	cat cracker feed
	1985	Esso Chemical	120	0	slop oil
			<u>1182</u>	<u>91</u>	
<u>Latex</u>	1975	Polysar	17	17	
	1976	Polysar	18	18	
	1980	Polysar	87	87	
	1980	Polysar	20	20	
			<u>142</u>	<u>142</u>	
<u>Styrene</u>	1974	Dow	4504	2700	
	1978	Polysar	411	80	
			<u>4915</u>	<u>2780</u>	
<u>Inorganic</u>	1974	Dow	21	21	hydrochloric acid
	1975	Dow	28	28	sodium hydroxide
	1979	Dow	4080	4000	sodium chlorate
	1981	Polysar	13	13	sulphuric acid
	1981	Dow	379	76	sodium chloride
	1982	Suncor	16	0	hydrochloric acid
	1983	Esso Chemical	19	4	sodium hydroxide
	1984	Esso Petroleum	164	33	brine
			<u>4720</u>	<u>4175</u>	
<u>Miscel- laneous</u>	1975	Polysar	159	33	lignin liquor
	1975	Esso Petroleum	239	239	phenolic waste water
	1975	Suncor	91	73	process water
	1975	Eagle Transport	11	2	xylene
	1976	Dow	13	0	ethylene glycol
	1982	Esso Petroleum	46	46	wash water
	1985	Dow	54	0	perchloroethylene
			<u>559</u>	<u>393</u>	

* Estimate based on reports of percent recovered.

APPENDIX I

DATA TABLES

TABLE 4-1

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
SAMPLING LOCATIONS

Facility	Sampling Site	Sample Type	Date Sampled	Time(s) Sampled
Esso Chemical Esso Petroleum	Intake	3 Grab Composite	26/11/85	1025, 1450, 1740
	Final Effluent*	3 Grab Composite	26/11/85	0955, 1425, 1705
	Biox Effluent**	3 Grab Composite	26/11/85	1005, 1440, 1720
Scott Road Landfill Scott Road Landfill Scott Road Landfill Township Ditch *** Township Ditch	Dow Scott Road Before Carbon	Single Grab	26/11/85	0930
	Dow Scott Road After Carbon	Single Grab	26/11/85	0915
	Scott Road Outfall (to Township Ditch)	3 Grab Composite	25/11/85	0840, 1140, 1620
	Before Polysar (water Vidal Street at Armak Chemicals Building)	3 Grab Composite	25/11/85	0800, 1130, 1610
	Before Polysar (sediment)	Single Grab	25/11/85	1045
Sarnia WPCP	Final Effluent*	3 Grab Composite	27/11/85	0800, 1050, 1500
Polysar Polysar Polysar Polysar Polysar	Intake	3 Grab Composite	27/11/85	0940, 1345, 1605
	Bio-Treatment Plant Effluent*	24 Hour Composite (Volatiles 3 Grab Composite)	27-28/11/85	1000 - 0900 0945, 1355, 1615
	54" Sewer*	3 Grab Composite	27/11/85	0925, 1340, 1600
	66" Sewer*	3 Grab Composite	27/11/85	0830, 1300, 1530
	72" Sewer*	3 Grab Composite	27/11/85	0905, 1315, 1540
	Stereo API****	3 Grab Composite	27/11/85	0845, 1330, 1550
Dow Chemical Dow Chemical Dow Chemical Dow Chemical Dow Chemical	Intake (North and South Pumphouses)	6 Grab Composite	27/11/85	NPH: 1030, 1300, 1645 SPH: 1050, 1350, 1710
	1st Street, 42" Sewer*	3 Grab Composite	27/11/85	0940, 1235, 1620
	1st Street, 48" Sewer*	3 Grab Composite	27/11/85	0950, 1240, 1630
	1st Street, 30" Acid Tile*	3 Grab Composite	27/11/85	0905, 1225, 1605
	1st Street, 54" Sluice* (Route of discharge for perchloroethylene spill)	24 Hour Composite (Volatiles 3 Grab Composite)	27-28/11/85	0925-0830 0925, 1220, 1610
Dow Chemical Dow Chemical Dow Chemical	2nd Street Sewer*	3 Grab Composite	27/11/85	1000, 1250, 1635
	3rd Street Sewer*	3 Grab Composite	27/11/85	1015, 1310, 1650
	4th Street Sewer*	3 Grab Composite	27/11/85	1045, 1325, 1700
Suncor Suncor	Intake (Directly from River)	3 Grab Composite	26/11/85	0910, 1345, 1630
	Impounding Basin Effluent**	3 Grab Composite	26/11/85	0850, 1330, 1615

* Actual discharge to the river.

** Combines with cooling water prior to discharging to the river.

*** Township Ditech ultimately discharges to the river after flowing through Polysar.

**** Discharges to 66" sewer downstream of sampling location.

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
DOW EFFLUENTS VS PERCHLOROETHYLENE PUDDLES¹

EPS-ONTARIO REGION SAMPLES NOVEMBER 27-28, 1985

Compound	% in PP2	1st Street 42" Sewer		1st Street 48" Sewer		1st Street 30" Acid Tile		1st Street 54" Sluice		2nd Street Sewer		3rd Street Sewer		4th Street Sewer	
		Conc. ug/l	%	Conc. ug/l	%	Conc. ug/l	%	Conc. ug/l	%	Conc. ug/l	%	Conc. ug/l	%	Conc. ug/l	%
Perchloroethylene	60+	100	51	2.9	62	710	25	27	47	4.6	53	1.2	1.2	1.8	51
Carbon Tetrachloride	30+	61	31	1.4	30	1,000	35	2.9	5.1	3.4	40	95	95	1.4	40
Hexachloroethane	0.8	2	1.0	0.0094	0.2	2.8	0.1	0.072	0.13	0.017	0.2	0.013	0.013	0.029	0.8
Hexachlorobutadiene	0.6	2.9	1.5	0.017	0.4	1.9	0.07	0.042	0.07	0.018	0.2	0.016	0.016	0.022	0.6
Hexachlorobenzene	0.4	1.4	0.7	0.018	0.4	2.8	0.1	0.020	0.04	0.0048	0.06	0.0092	0.0092	0.024	0.7
1,1,1-Trichloroethane	0.5	-	0	-	0	710	25	19	33	-	0	-	-	-	0
Trichloroethylene	0.3	9.4	4.8	-	0	230	8.1	4.1	7.2	-	0	-	-	-	0
Octachlorostyrene	0.02	0.041	0.02	0.0013	0.03	0.16	<0.01	0.0017	<0.01	0.0007	<0.01	0.0007	<0.01	0.0016	0.05
Pentachlorobenzene	0.01	0.046	0.02	0.0006	0.01	0.10	<0.01	0.0013	<0.01	0.0006	<0.01	0.0061	<0.01	0.0012	0.05
Tetrachlorobenzenes	0.02	0.037	0.02	-	0	0.108	<0.01	-	0	0.0094	0.11	0.0056	<0.01	-	0
Trichlorobenzenes	0.01	6.0	3.1	0.020	0.43	4.8	0.17	0.090	0.16	0.091	1.0	0.028	0.03	0.022	0.6
Total Concentrations		182.8		4.366		2,663		53.22		8.141		96.26		3.284	
		x 1.07		x 1.07		x 1.07		x 1.07		x 1.07		x 1.07		x 1.07	
TOTAL	93	195.6	93	4.672	93	2849	93	56.95	93	8.711	93	103.0	93	3.531	93

¹ Total concentrations multiplied by 1.07 for calculating percentages.

² Perchloroethylene Puddles

TABLE 4-3

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
VOLATILE ORGANICS (ug/l)

PARAMETERS ²	MDL ¹	Esso Intake	Esso Petroleum Blox	Esso Chemical Final Effluent	Suncor Intake	Suncor Impounding Basin	Sarnia WPOP
Chloroethane	2	-	-	-	-	-	-
Vinyl Chloride	2	-	-	66	-	-	-
Methylene Chloride	1	-	-	-	<1.0	-	3.3
1,1-Dichloroethane	1	-	-	-	-	-	<1.0
1,1-Dichloroethane	1	-	-	-	-	-	<1.0
Trans-1,2-Dichloroethane	1	-	-	-	-	-	1.9
Chloroform	1	-	<1.0	<1.0	<1.0	9.1	4.9
1,2-Dichloroethane	1	-	-	5.7	1.0	64	-
1,1,1-Trichloroethane	1	-	-	3.5	2.0	30	1.6
Carbon Tetrachloride	1	-	-	-	3.5	-	-
Bromodichloromethane	1	-	-	-	-	-	-
1,2-Dichloropropane	1	-	-	-	1.1	-	-
Trichloroethane	1	-	<1.0	-	<1.0	-	2.6
Benzene	1	-	-	-	23	64	13
Dibromochloromethane	1	-	-	-	-	-	-
1,1,2-Trichloroethane	1	-	-	-	-	-	-
2-Chloroethyl Vinyl Ether	2	-	-	-	-	-	-
Bromoform	1	-	-	-	-	-	-
Tetrachloroethene*	1	-	-	-	5.6	1.2	3.7
1,1,2,2-Tetrachloroethane	1	-	-	-	-	-	<1.0
Toluene	1	-	-	-	<1.0	4.3	1.3
Chlorobenzene	1	-	-	-	-	1.0	-
Ethylbenzene	1	-	-	-	1.4	<1.0	1.5
Acrolein	5	-	-	-	<5.0	-	-
Acrylonitrile	5	-	-	-	-	-	-
3-Chloropropene	2	-	-	-	-	-	-
1,2-Dibromomethane	1	-	-	-	-	-	-
Meta + para xylene	1	1.2	-	-	<1.0	200	<1.0
Styrene	1	-	-	-	1.1	-	3.3
Ortho xylene	1	<1.0	-	-	<1.0	230	3.0
Pentachloroethane	1	-	-	-	-	-	-

* Perchloroethylene

1 MDL = Method Detection Limit; "-" Indicates not detected; "<x" Indicates peak present below MDL;

2 Also analysed but not detected (MDL in Brackets): chloromethane (2), Bromoethane (2), cis-1,3-dichloropropene (2), trans-1,3-dichloropropene (2), trichlorofluoromethane (2), 1,1,2-Trifluorotrichloroethane (1), dichloroacetonitrile (5), 1-Bromo-2-chloroethane (1), bromobenzene (1), 1,1,2,3-tetrachloropropene (2).

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
VOLATILE ORGANICS (ug/l)

PARAMETERS ²	MDL ¹	Polysar Intake	Polysar Bio-Treatment Plant	Polysar 72" Sewer	Polysar 66" Sewer	Polysar 54" Sewer	Polysar Stereo API 3
Chloroethane	2	-	-	-	-	-	-
Vinyl Chloride	2	-	-	-	-	-	-
Methylene Chloride	1	-	-	<1.0	-	-	1.8
1,1-Dichloroethane	1	-	-	-	-	-	-
Trans-1,2-Dichloroethane	1	-	-	-	-	-	-
Chloroform	1	-	1.8	<1.0	<1.0	<1.0	1.2
1,2-Dichloroethane	1	<1.0	-	-	1.4	-	-
1,1,1-Trichloroethane	1	-	<1.0	-	-	-	-
Carbon Tetrachloride	1	-	-	-	-	-	-
Bromodichloromethane	1	-	-	<1.0	-	-	<1.0
1,2-Dichloropropane	1	-	-	-	-	-	-
Trichloroethane	1	-	<1.0	-	-	-	-
Benzene	1	-	-	4,000	9.2	<1.0	500
Dibromochloromethane	1	-	-	<1.0	-	-	-
1,1,2-Trichloroethane	1	-	-	-	-	-	<1.0
2-Chloroethyl Vinyl Ether	2	-	-	-	-	<2.0	-
Bromoform	1	-	38	-	-	-	-
Tetrachloroethene*	1	<1.0	<1.0	-	-	-	-
1,1,2,2-Tetrachloroethane	1	-	-	<1.0	-	-	-
Toluene	1	<1.0	-	-	2.6	<1.0	<1.0
Chlorobenzene	1	-	-	-	-	-	-
Ethylbenzene	1	<1.0	-	-	3.1	-	2.7
Acrolein	5	-	-	-	-	7.8	-
Acrylonitrile	5	-	-	-	-	-	-
3-Chloropropene	2	-	-	-	-	-	-
1,2-Dibromoethane	1	-	-	-	-	-	-
Meta + para xylene	1	<1.0	-	<1.0	<1.0	-	-
Styrene	1	-	-	-	<1.0	-	2.8
Ortho xylene	1	<1.0	-	-	<1.0	-	-
Pentachloroethane	1	-	-	-	-	-	-

* Perchloroethylene

1 MDL = Method Detection Limit; "-" indicates not detected; "<x" indicates peak present below MDL;

2 Also analysed but not detected (MDL in Brackets): chloromethane (2), Bromoethane (2), cis-1,3-dichloropropene (2), trans-1,3-dichloropropene (2), trichlorofluoromethane (2), 1,1,2-Trifluorotrchloroethane (1), dichloroacetonitrile (5), 1-Bromo-2-chloroethane (1), bromobenzene (1), 1,1,2,3-tetrachloropropene (2).

3 Stereo API effluent discharges to the 66" sewer, downstream of 66" sewer sampling location.

TABLE 4-5

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
VOLATILE ORGANICS (ug/l)

PARAMETERS ²	MDL ¹	Down Intake North and South Pumphouses Composite	1st Street 42nd Sewer	1st Street 48th Sewer	1st Street 30th Acid Tille	1st Street 54th Sewer	2nd Street Sewer	3rd Street Sewer	4th Street Sewer
Chloroethane	2	-	-	-	-	-	-	-	-
Vinyl Chloride	2	-	<2.0	-	-	<2.0	-	-	-
Methylene Chloride	1	-	<1.0	-	22	<1.0	2.4	1.5	-
1,1-Dichloroethane	1	-	11	<1.0	530	4.4	-	-	-
1,1-Dichloroethane	1	-	5.5	<1.0	470	11	-	<1.0	-
Trans-1,2-Dichloroethane	1	-	-	-	-	-	-	-	-
Chloroform	1	<1.0	17	<1.0	42	1.1	1.1	-	<1.0
1,2-Dichloroethane	1	<1.0	140	2.2	920	17	1.2	-	-
1,1,1-Trichloroethane	1	<1.0	-	<1.0	710	19	-	<1.0	-
Carbon Tetrachloride	1	1.9	61	1.4	1,000	29	3.4	95	1.4
Bromodichloromethane	1	-	-	-	-	-	-	-	-
1,2-Dichloropropane	1	<1.0	5.6	<1.0	60	310	22	<1.0	-
Trichloroethane	1	-	9.4	-	230	4.1	-	<1.0	-
Benzene	1	3.1	3.9	<1.0	4.4	<1.0	-	490	10
Dibromochloromethane	1	-	-	-	-	-	-	-	-
1,1,2-Trichloroethane	1	-	26	-	180	2.1	-	-	-
2-Chloroethyl Vinyl Ether	2	-	-	-	-	-	-	-	-
Bromoform	1	-	-	-	-	-	-	-	-
Tetrachloroethane*	1	3.5	100	2.9	710	27	4.6	1.2	1.8
1,1,2,2-Tetrachloroethane	1	-	14	-	31	-	-	-	-
Toluene	1	-	<1.0	-	<1.0	<1.0	-	28	1.3
Chlorobenzene	1	-	-	-	<1.0	-	-	-	-
Ethylbenzene	1	-	<1.0	-	<1.0	<1.0	-	500	17
Acrolein	5	-	-	-	-	-	-	-	6.9
Acrylonitrile	5	-	-	-	-	-	-	-	5.2
3-Chloropropene	2	-	-	-	-	-	-	-	-
1,2-Dibromoethane	1	-	<1.0	-	-	-	-	-	-
Meta + para xylene	1	-	<1.0	-	<1.0	<1.0	-	-	-
Styrene	1	-	-	-	-	-	-	970	23
Ortho xylene	1	-	<1.0	-	<1.0	<1.0	-	6.4	-
Pentachloroethane	1	-	<1.0	-	1.2	-	-	-	-

* Perchloroethylene

¹ MDL = Method Detection Limit; "-" Indicates not detected; "<x" Indicates peak present below MDL² Also analysed but not detected (MDL in Brackets): chloromethane (2), Bromoethane (2), cis-1,3-dichloropropene (2), trans-1,3-dichloropropene (2), trichlorofluoromethane (2), 1,1,2-trifluorotrchloroethane (1), dichloroacetonitrile (5), 1-bromo-2-chloroethane (1), bromobenzene (1), 1,1,2,3-tetrachloropropene (2).

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
VOLATILE ORGANICS (ug/l)

PARAMETERS ²	MDL ¹	Dow Scott Road Before Carbon (Not a Discharge)	Dow Scott Road After Carbon	Scott Road Outfall	Township Ditch Before Polysar
Chloroethane	2	28	-	-	-
Vinyl Chloride	2	-	-	-	-
Methylene Chloride	1	9.7	160	3.2	<1.0
1,1-Dichloroethane	1	170	73	1.8	-
1,1-Dichloroethane	1	360	1,900	65	3.6
Trans-1,2-Dichloroethane	1	-	-	-	-
Chloroform	1	250	950	48	27
1,2-Dichloroethane	1	6,100	39,000	910	64
1,1,1-Trichloroethane	1	-	240	-	-
Carbon Tetrachloride	1	1,000	-	-	-
Bromodichloromethane	1	-	-	-	-
1,2-Dichloropropane	1	320	510	41	2.0
Trichloroethane	1	650	780	11	1.7
Benzene	1	25	-	-	<1.0
Dibromochloromethane	1	-	-	-	-
1,1,2-Trichloroethane	1	1,300	1,800	100	5.6
2-Chloroethyl Vinyl Ether	2	-	-	-	-
Bromoform	1	-	-	-	-
Tetrachloroethane*	1	1,800	37	17	3.3
1,1,2,2-Tetrachloroethane	1	140	93	6.6	2.2
Toluene	1	8.8	-	<1.0	<1.0
Chlorobenzene	1	-	-	-	-
Ethylbenzene	1	130	<1.0	-	-
Acrolein	5	<5.0	-	-	-
Acrylonitrile	5	-	-	-	-
3-Chloropropene	2	2.3	-	-	-
1,2-Dibromoethane	1	-	-	-	-
Meta + para xylene	1	-	-	-	-
Styrene	1	67	-	-	-
Ortho xylene	1	3.8	-	-	-
Pentachloroethane	1	-	-	-	-

* Perchloroethylene

1 MDL = Method Detection Limit; "-" Indicates not detected; "<x" Indicates peak present below MDL;

2 Also analysed but not detected (MDL in brackets): chloromethane (2), Bromoethane (2), cis-1,3-dichloropropene (2), trans-1,3-dichloropropene (2), trichlorofluoromethane (2), 1,1,2-Trifluoro-1,1,2,2-tetrachloroethane (1), dichloroacetonitrile (5), 1-Bromo-2-chloroethane (1), bromobenzene (1), 1,1,2,3-tetrachloropropene (2).

TABLE 4-7
ST. CLAIR STUDY - POINT SOURCE DISCHARGES
VOLATILE ORGANICS - NET LOADINGS (Kg/d)

PARAMETERS ²	MDL	Esso Petroleum Blox 20.1 x 10 ⁶ l/d	Esso Chemical Final 34.5 x 10 ⁶ l/d	Suncor Impounding Basin 7.86 x 10 ⁶ l/d	Polysar Bio- Treatment Plant 12.0 x 10 ⁶ l/d	Polysar 72" Sewer 26.3 x 10 ⁶ l/d	Polysar 66" Sewer 163 x 10 ⁶ l/d	Polysar 54" Sewer 58 x 10 ⁶ l/d	Polysar Stereo API 3.22x10 ⁶ l/d	Sarnia WQOP 59x10 ⁶ l/d
Chloroethane	2	-	-	-	-	-	-	-	-	-
Vinyl Chloride	2	-	2.3	-	-	-	-	-	-	-
Methylene Chloride	1	-	-	-	-	<0.026	-	-	0.0058	0.19
1,1-Dichloroethane	1	-	-	-	-	-	-	-	-	<0.059
1,1-Dichloroethane	1	-	-	-	-	-	-	-	-	<0.059
Trans-1,2-Dichloroethane	1	-	-	-	-	-	-	-	-	0.11
Chloroform	1	<0.020	<0.035	0.071	0.022	0.026	<0.16	<0.058	0.0039	0.29
1,2-Dichloroethane	1	-	0.20	0.49	-	-	0.23	-	-	-
1,1,1-Trichloroethane	1	-	0.12	0.22	<0.012	-	-	-	-	0.094
Carbon Tetrachloride	1	-	-	-	-	-	-	-	-	-
Bromodichloromethane	1	-	-	-	-	<0.026	-	-	<0.0032	-
1,2-Dichloropropane	1	-	-	-	<0.012	-	-	-	-	0.15
Trichloroethane	1	<0.020	-	-	-	110	1.5	<0.058	1.6	0.77
Benzene	1	-	-	0.32	-	<0.026	-	-	-	-
Dibromochloromethane	1	-	-	-	-	-	-	-	-	-
1,1,2-Trichloroethane	1	-	-	-	-	-	-	-	<0.0032	-
2-Chloroethyl Vinyl Ether	2	-	-	-	0.46	-	-	<0.12	-	-
Bromoform	1	-	-	-	-	-	-	-	-	-
Tetrachloroethane*	1	-	-	-	-	-	-	-	-	0.22
1,1,2,2-Tetrachloroethane	1	-	-	-	-	<0.026	-	-	-	<0.059
Toluene	1	-	-	0.034	-	-	0.42	-	-	0.077
Chlorobenzene	1	-	-	0.0079	-	-	-	-	-	-
Ethylbenzene	1	-	-	-	-	-	0.51	-	0.0064	0.089
Acrolein	5	-	-	-	-	-	-	0.45	-	-
Acrylonitrile	5	-	-	-	-	-	-	-	-	-
3-Chloropropene	2	-	-	-	-	-	-	-	-	-
1,2-Dibromoethane	1	-	-	-	-	-	-	-	-	<0.059
Meta + para xylene	1	-	-	1.6	-	-	-	-	-	0.19
Styrene	1	-	-	-	-	-	-	-	0.0090	-
Ortho xylene	1	-	-	1.8	-	-	-	-	-	0.18
Pentachloroethane	1	-	-	-	-	-	-	-	-	-

* Perchloroethylene ¹ MDL = Method Detection Limit; "-" Indicates not detected; "x" Indicates peak present below MDL;

² Also analysed but not detected (MDL in Brackets): chloromethane (2), Bromoethane (2), cis-1,3-dichloropropene (2), trans-1,3-dichloropropene (2), trichlorofluoromethane (2), 1,1,2-Trifluorotrichloroethane (1), dichloroacetonitrile (5), 1-Bromo-2-chloro ethane (1), Bromobenzene (1), 1,1,2,3-tetrachloropropene (2).

TABLE 4-8

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
VOLATILE ORGANICS - NET LOADINGS (Kg/d)

PARAMETERS ²	MDL ¹ (ug/l)	1st Street 42" Sewer 65x10 ⁶ l/d	1st Street 48" Sewer 56x10 ⁶ l/d	1st Street 30" Acid Tille 10 x 10 ⁶ l/d	1st Street 54" Sewer 30x10 ⁶ l/d	2nd Street Sewer 66x10 ⁶ l/d	3rd Street Sewer 120x10 ⁶ l/d	4th Street Sewer 565x10 ⁶ l/d
Chloroethane	2	-	-	-	-	-	-	-
Vinyl Chloride	2	<0.13	-	-	<0.060	-	-	-
Methylene Chloride	1	<0.065	-	0.22	<0.030	0.16	0.18	-
1,1-Dichloroethane	1	0.71	<0.056	5.3	0.13	-	-	-
1,1,1-Dichloroethane	1	0.36	<0.056	4.7	0.33	-	<0.12	-
Trans-1,2-Dichloroethane	1	-	-	-	-	-	-	-
Chloroform	1	1.1	-	0.42	-	-	-	<0.57
1,2-Dichloroethane	1	9.1	0.12	9.2	0.51	-	-	-
1,1,1-Trichloroethane	1	-	-	7.1	0.57	-	<0.12	-
Carbon Tetrachloride	1	3.8	-	10	0.81	0.099	11	-
Bromodichloromethane	1	-	-	-	-	-	-	-
1,2-Dichloropropane	1	0.36	-	0.6	9.3	1.5	<0.12	-
Trichloroethane	1	0.61	-	2.3	0.12	-	<0.12	-
Benzene	1	0.052	-	0.044	-	-	58	3.9
Dibromochloromethane	1	-	-	-	-	-	-	-
1,1,2-Trichloroethane	1	1.7	-	1.8	0.063	-	-	-
2-Chloroethyl Vinyl Ether	2	-	-	-	-	-	-	-
Bromoform	1	-	-	-	-	-	-	-
Tetrachloroethane*	1	6.3	-	7.1	0.71	0.073	-	-
1,1,2,2-Tetrachloroethane	1	0.91	-	0.3	-	-	-	-
Toluene	1	<0.065	-	<0.010	<0.030	-	3.4	0.73
Chlorobenzene	1	-	-	<0.010	-	-	-	-
Ethylbenzene	1	<0.065	-	<0.010	<0.030	-	60	9.6
Acrolein	5	-	-	-	-	-	-	3.9
Acrylonitrile	5	-	-	-	-	-	-	2.9
3-Chloropropene	2	-	-	-	-	-	-	-
1,2-Dibromoethane	1	<0.065	-	-	-	-	-	-
Meta + para xylene	1	<0.065	-	<0.010	<0.030	-	-	-
Styrene	1	-	-	-	-	-	120	13
Ortho xylene	1	<0.065	-	<0.010	<0.030	-	-	-
Pentachloroethane	1	<0.065	-	0.010	-	-	-	-

* Perchloroethylene

1 MDL = Method Detection Limit; "-" indicates not detected; "<x" indicates peak present below MDL;

2 Also analysed but not detected (MDL in Brackets): chloromethane (2), bromoethane (2), cis-1,3-dichloropropene (2), trans-1,3-dichloropropene (2), trichlorofluoromethane (2), 1,1,2-trifluoro-1,1,2,2-tetrachloroethane (1), dichloroacetonitrile (5), 1-bromo-2-chloroethane (1), bromobenzene (1), 1,1,2,3-tetrachloropropene (2).

TABLE 4-9

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
EXTRACTABLE CHLORINATED ORGANICS (ug/l)

PARAMETERS	MDL ¹	Esso Intake	Esso Petroleum Blox	Esso Chemical Final Effluent	Suncor Intake	Suncor Impounding Basin	Sarnia WPCP
1,3-Dichlorobenzene	0.050	-	-	-	-	0.079	0.082
1,4-Dichlorobenzene	0.10	-	0.017	-	-	0.045	0.090
1,2-Dichlorobenzene	0.050	-	0.019	-	-	0.20	0.11
1,3,5-Trichlorobenzene	0.006	-	-	0.011	0.009	0.025	0.012
1,2,4-Trichlorobenzene	0.007	-	-	0.029	0.042	0.026	0.017
1,2,3-Trichlorobenzene	0.004	-	-	-	-	0.0056	-
1,2,3,5-Tetrachlorobenzene	0.002	-	-	-	0.0054	-	-
1,2,4,5-Tetrachlorobenzene	0.004	-	0.013	-	-	0.012	-
1,2,3,4-Tetrachlorobenzene	0.002	-	-	-	0.0032	0.0031	-
Pentachlorobenzene	0.001	-	-	-	-	0.0026	-
Hexachlorobenzene	0.001	0.0061	0.0025	0.0047	0.010	0.025	0.0031
Hexachloroethane	0.001	-	0.0003	0.030	0.026	0.0057	0.0033
Hexachlorobutadiene	0.001	0.0015	0.0005	0.035	0.027	0.0034	0.0047
Octachlorostyrene	0.001	0.0008	0.0005	0.0028	0.0012	0.0006	-
α-Benzene Hexachloride	0.001	0.0025	-	0.0023	0.0028	0.0029	0.0008
Lindane	0.001	-	-	0.0006	-	-	0.011
V-Chlorane	0.002	-	-	-	-	-	-
p,p,'-DDE	0.002	-	-	-	-	-	-
p,p,'-DDD	0.002	-	-	-	-	-	-
p,p,'-DDT	0.005	-	-	-	-	-	-
Mirex	0.006	-	-	-	-	-	-
Total PCB's	0.02	-	-*	-	-	-*	-

¹ MDL = Method Detection Limit; "-" Indicates not detected; Numbers reported below the MDL should be considered tentative.

* Detected in preliminary analysis, quantity not confirmed in subsequent analysis.

TABLE 4-10

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
EXTRACTABLE CHLORINATED ORGANICS (ug/l)

PARAMETERS	MDL ¹	Polysar Intake	Polysar Bio-treatment Plant	Polysar 72" Sewer	Polysar 66" Sewer	Polysar 54" Sewer	Polysar Stereo API 2
1,3-Dichlorobenzene	0.050	-	0.015	-	-	-	-
1,4-Dichlorobenzene	0.10	0.28	-	-	-	-	-
1,2-Dichlorobenzene	0.050	-	-	-	0.028	-	-
1,3,5-Trichlorobenzene	0.006	-	-	-	0.005	-	-
1,2,4-Trichlorobenzene	0.007	-	0.0085	-	-	-	-
1,2,3-Trichlorobenzene	0.004	-	-	-	-	-	-
1,2,3,5-Tetrachlorobenzene	0.002	-	-	-	-	-	-
1,2,4,5-Tetrachlorobenzene	0.004	-	-	-	-	-	-
1,2,3,4-Tetrachlorobenzene	0.002	-	-	-	-	-	-
Pentachlorobenzene	0.001	0.0013	-	0.0009	-	-	0.0005
Hexachlorobenzene	0.001	0.0088	0.0022	0.0041	0.0025	0.0014	0.0014
Hexachloroethane	0.001	0.0019	0.0003	0.0010	0.0008	0.0012	0.0015
Hexachlorobutadiene	0.001	0.059	0.0026	0.021	0.014	0.019	0.018
Octachlorostyrene	0.001	0.0021	-	0.0020	-	0.0007	0.0008
α-Benzene Hexachloride	0.001	0.0025	0.0003	0.0026	0.0025	0.0027	0.0024
Lindane	0.001	0.0005	-	0.0005	-	0.0006	0.0005
v-Chlorane	0.002	-	-	-	-	-	-
p,p',i-DDE	0.002	-	-	-	-	-	-
p,p',i-DDD	0.002	-	-	-	-	-	-
p,p',i-DDT	0.005	-	-	-	-	-	-
Mirex	0.006	-	-	-	-	-	-
Total PCB's	0.02	-	-	-	-	-	-

¹ MDL = Method Detection Limit; "-" indicates not detected; Numbers reported below the detection limit should be considered tentative.

² Discharges to 66" sewer upstream of sampling location.

TABLE 4-11

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
EXTRACTABLE CHLORINATED ORGANICS (ug/l)

PARAMETERS	MDL ¹	DOW INTAKE NORTH & SOUTH PUMPHOUSES COMPOSITE	1ST STREET 42" SEWER	1ST STREET 48" SEWER	1ST STREET 30" ACID TILE	1ST STREET 54" SEWER	2ND STREET SEWER	3RD STREET SEWER	4TH STREET SEWER
1,3-Dichlorobenzene	0.050	-	-	-	-	-	-	-	-
1,4-Dichlorobenzene	0.10	-	0.52	-	0.47	-	-	-	-
1,2-Dichlorobenzene	0.050	-	0.047	-	0.042	-	0.30	-	-
1,3,5-Trichlorobenzene	0.006	-	0.11	-	0.27	-	0.0070	0.0033	-
1,2,4-Trichlorobenzene	0.007	0.036	5.9	0.020	4.3	0.090	0.084	0.019	0.022
1,2,3-Trichlorobenzene	0.004	-	0.0080	-	0.0014	-	0.0058	0.0058	-
1,2,3,5-Tetrachlorobenzene	0.002	-	0.011	-	0.029	-	0.0043	0.0027	-
1,2,4,5-Tetrachlorobenzene	0.004	-	-	-	0.017	-	-	-	-
1,2,3,4-Tetrachlorobenzene	0.002	-	0.026	-	0.061	-	0.0051	0.0029	-
Pentachlorobenzene	0.001	0.0013	0.046	0.0006	0.10	0.0013	0.0006	0.0061	0.0012
Hexachlorobenzene	0.001	0.0046	1.4	0.018	2.8	0.020	0.0048	0.0092	0.024
Hexachloroethane	0.001	0.019	2.0	0.0094	2.8	0.072	0.017	0.013	0.029
Hexachlorobutadiene	0.001	0.052	2.9	0.017	1.9	0.042	0.018	0.016	0.022
Octachlorostyrene	0.001	0.0029	0.041	0.0013	0.16	0.0017	0.0007	0.0007	0.0016
α-Benzene Hexachloride	0.001	0.0026	0.0083	0.0027	0.0018	0.0023	0.0025	0.0055	0.0027
Linsanl	0.001	0.0005	0.0028	0.0005	0.0016	0.0005	0.0005	0.0008	0.0006
γ-Chlorane	0.002	-	-	-	0.0038	-	-	-	-
p,p'-DDE	0.002	-	-	-	-	-	-	-	-
p,p'-DDD	0.002	-	-	-	-	-	-	-	-
p,p'-DDT	0.005	-	-	-	-	-	-	-	-
Mirex	0.006	-	-	-	-	-	-	-	-
Total PCB's	0.02	-*	-*	-*	-*	-	-	0.042	-

¹ MDL = Method Detection Limit; "-" Indicates not detected; Numbers reported below the detection limit should be considered tentative.

*Detected in preliminary analysis, quantity not confirmed in subsequent analysis.

TABLE 4-12

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
EXTRACTABLE CHLORINATED ORGANICS (ug/l)

PARAMETERS	MDL ¹	DOW SCOTT ROAD BEFORE CARBON (NOT DISCHARGED)	DOW SCOTT ROAD AFTER CARBON	SCOTT ROAD OUTFALL	TOWNSHIP DITCH BEFORE POLYSAR WATER	TOWNSHIP DITCH BEFORE POLYSAR SEDIMENT 2
1,3-Dichlorobenzene	0.050	0.14	0.066	-	-	24
1,4-Dichlorobenzene	0.10	19	0.26	13	5.0	63,000
1,2-Dichlorobenzene	0.050	0.78	0.010	-	-	6,600
1,3,5-Trichlorobenzene	0.006	8.4	0.045	0.031	0.17	1,900
1,2,4-Trichlorobenzene	0.007	17	1.4	7.7	2.3	2,600
1,2,3-Trichlorobenzene	0.004	0.025	0.010	0.0038	0.0082	6.4
1,2,3,5-Tetrachlorobenzene	0.002	0.98	0.005	0.027	0.020	470
1,2,4,5-Tetrachlorobenzene	0.004	-	0.018	-	0.0075	350
1,2,3,4-Tetrachlorobenzene	0.002	0.36	0.004	-	0.010	130
Pentachlorobenzene	0.001	1.6	0.052	0.012	0.023	1,700
Hexachlorobenzene	0.001	5.6	0.22	0.015	0.018	4,700
Hexachloroethane	0.001	120	0.025	0.59	0.41	490
Hexachlorobutadiene	0.001	94	6.7	0.88	1.5	98,000
Octachlorostyrene	0.001	2.3	0.21	0.0026	0.0042	3,000
α-Benzene Hexachloride	0.001	0.020	0.0027	0.0014	0.0015	4.0
Linsanl	0.001	0.011	-	-	-	4.9
v-Chlorane	0.002	0.0011	0.0008	-	-	-
p,p',1-DDE	0.002	0.0031	-	-	-	1.9
p,p',1-DDD	0.002	0.0006	0.0004	-	-	1.0
p,p',1-DDT	0.005	0.0064	0.0011	-	-	6.0
Mirex	0.006	-	-	-	-	-
Total PCB's	0.02	-*	-*	-	-	440

1 MDL = Method Detection Limit; "-" indicates not detected; Numbers reported below the detection limit should be considered tentative.

* Detected in preliminary analysis, quantity not confirmed in subsequent analysis.

TABLE 4-13

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
CHLOROPHENOLS AND CHLOROPHENOXY ACIDS (ug/l)

PARAMETERS	MDL ¹	ESSO INTAKE	ESSO PETROLEUM BIOX	ESSO CHEMICAL FINAL EFFLUENT	SUNCOR INTAKE	SUNCOR IMPOUNDING BASIN	SARNIA WPCP
2,6-Dichlorophenol	0.001	-	-	-	-	-	-
2,4-Dichlorophenol	0.001	-	-	-	-	-	-
2,3-Dichlorophenol	0.001	-	0.15	-	-	-	-
2,4,6-Trichlorophenol	0.003	-	-	-	0.010	-	0.037
2,3,6-Trichlorophenol	0.001	-	-	-	-	-	-
2,4,5-Trichlorophenol	0.001	-	-	-	-	-	-
2,3,5-Trichlorophenol	0.001	-	-	-	-	-	-
3,4,5-Trichlorophenol	0.001	-	-	-	-	-	-
2,3,5,6-Tetrachlorophenol	0.001	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.001	-	-	-	-	-	0.053
2,3,4,5-Tetrachlorophenol	0.001	-	-	-	-	-	0.006
Pentachlorophenol	0.001	0.002	0.003	0.005	0.005	0.014	0.057
2,4-D	0.001	-	-	-	-	-	-
2,4,5-T	0.001	-	-	-	-	-	-

¹ MDL = Method Detection Limit; "-" Indicates not detected.

TABLE 4-14

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
CHLOROPHENOLS AND CHLOROPHENOXY ACIDS (ug/l)

PARAMETERS	MDL ¹	POLYSAR INTAKE	POLYSAR BIO- TREATMENT PLANT	POLYSAR 72" SEWER	POLYSAR 66" SEWER	POLYSAR 54" SEWER	POLYSAR STEREO API 2
2,6-Dichlorophenol	0.001	-	-	-	-	-	-
2,4-Dichlorophenol	0.001	-	-	-	0.051	-	-
2,3-Dichlorophenol	0.001	-	-	-	-	-	-
2,4,6-Trichlorophenol	0.003	0.033	-	0.59	0.011	-	0.10
2,3,6-Trichlorophenol	0.001	-	-	-	-	-	-
2,4,5-Trichlorophenol	0.001	-	-	-	0.020	-	-
2,3,5-Trichlorophenol	0.001	-	-	-	-	-	-
3,4,5-Trichlorophenol	0.001	-	-	-	-	-	-
2,3,5,6-Tetrachlorophenol	0.001	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.001	-	0.002	-	0.004	-	0.003
2,3,4,5-Tetrachlorophenol	0.001	-	-	-	-	-	-
Pentachlorophenol	0.001	0.004	0.012	0.004	0.004	0.001	0.003
2,4-D	0.001	-	-	-	0.025	-	-
2,4,5-T	0.001	-	-	-	-	-	-

¹ MDL = Method Detection Limit; "-" indicates not detected;

² Discharges to 66" sewer downstream of sampling location.

TABLE 4-15

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
CHLOROPHENOLS AND CHLOROPHENOXY ACIDS (ug/l)

PARAMETERS	MDL ¹	DOW INTAKE NORTH AND PUMPHOUSES COMPOSITE	1st STREET 42" SEWER	1st STREET 48" SEWER	1st STREET 30" ACID TILE	2nd STREET SEWER	3rd STREET SEWER	4th STREET SEWER
2,6-Dichlorophenol	0.001	-	-	-	0.17	-	-	-
2,4-Dichlorophenol	0.001	-	-	-	0.54	-	-	-
2,3-Dichlorophenol	0.001	-	-	-	-	-	-	-
2,4,6-Trichlorophenol	0.003	0.006	0.018	0.004	0.12	-	-	0.013
2,3,6-Trichlorophenol	0.001	-	-	-	-	-	-	-
2,4,5-Trichlorophenol	0.001	-	-	-	-	-	-	-
2,3,5-Trichlorophenol	0.001	-	-	-	-	-	-	-
3,4,5-Trichlorophenol	0.001	-	-	-	-	-	-	-
2,3,5,6-Tetrachlorophenol	0.001	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.001	0.001	0.041	0.002	0.047	-	-	-
2,3,4,5-Tetrachlorophenol	0.001	-	-	-	-	-	-	-
Pentachlorophenol	0.001	0.003	0.018	0.006	0.10	0.004	0.004	0.006
2,4-D	0.001	-	-	-	0.094	-	-	-
2,4,5-T	0.001	-	-	-	-	-	-	-

¹ MDL = Method Detection Limit; "-" Indicates not detected;

TABLE 4-16

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
CHLOROPHENOLS AND CHLOROPHENOXY ACIDS (ug/l)

PARAMETERS	MDL ¹	DOW SCOTT ROAD BEFORE CARBON (NOT DISCHARGED)	DOW SCOTT ROAD AFTER CARBON	SCOTT ROAD OUTFALL	TOWNSHIP DITCH BEFORE POLYSAR WATER	TOWNSHIP DITCH BEFORE POLYSAR SEDIMENT
2,6-Dichlorophenol	0.001	7.3	-	0.12	-	-
2,4-Dichlorophenol	0.001	38	-	-	-	-
2,3-Dichlorophenol	0.001	-	-	-	-	-
2,4,6-Trichlorophenol	0.003	17	-	0.17	-	1.0
2,3,6-Trichlorophenol	0.001	0.70	-	0.020	-	0.9
2,4,5-Trichlorophenol	0.001	57	-	-	-	1.3
2,3,5-Trichlorophenol	0.001	-	-	0.054	-	0.25
3,4,5-Trichlorophenol	0.001	-	-	-	-	-
2,3,5,6-Tetrachlorophenol	0.001	-	-	-	-	0.26
2,3,4,6-Tetrachlorophenol	0.001	6.6	<0.010	0.012	-	0.68
2,3,4,5-Tetrachlorophenol	0.001	-	-	-	-	0.63
Pentachlorophenol	0.001	0.74	<0.010	0.005	0.004	0.58
2,4-D	0.001	21	18	0.41	-	-
2,4,5-T	0.001	1.7	1.0	0.028	-	-

¹ MDL = Method Detection Limit; for Sediment MDLs, Multiply by 10; "-" Indicates not detected;

² Except sediment, ug/Kg.

TABLE 4-17

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
PAHS (POLY AROMATIC HYDROCARBONS) (ug/l)

PARAMETERS	MDL ¹	ESSO INTAKE	ESSO PETROLEUM BIOX	ESSO CHEMICAL OUTFALL	SUNCOR INTAKE	SUNCOR IMPOUNDING BASIN	SARNIA WPCP
Naphthalene	0.01	0.19	0.18	0.35	0.20	23	0.57
Acenaphthylene	0.01	-	1.3	1.9	-	0.28	0.56
Acenaphthene	0.01	-	0.017	0.082	-	0.89	0.072
Fluorene	0.01	-	0.080	0.14	-	1.9	0.20
Phenanthrene	0.01	0.040	0.036	0.22	0.040	2.3	0.28
Anthracene	0.01	-	0.37	0.14	-	0.13	0.080
Fluoranthene	0.01	-	0.35	0.26	0.021	0.12	0.074
Pyrene	0.01	-	0.064	0.64	0.014	0.36	0.083
Benzo (a) Anthracene	0.01	-	0.026	0.16	-	0.11	0.010
Chrysene	0.01	-	0.045	0.28	-	0.34	0.012
Benzo (b) Fluoranthene	0.02	-	0.028	0.087	-	0.19	-
Benzo (k) Fluoranthene	0.02	-	-	0.028	-	0.030	-
Benzo (a) Pyrene	0.02	-	0.086	0.36	-	0.34	-
Indeno Pyrene	0.05	-	-	0.50	-	0.23	-
Dibenzo (a,h) Anthracene	0.05	-	-	0.30	-	0.40	-
Benzo (g,h,i) Perylene	0.05	-	0.17	0.65	-	0.12	-

¹ MDL = method Detection Limit; "-" indicates not detected;

TABLE 4-18

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
PAHs (POLY AROMATIC HYDROCARBONS) (ug/l)

PARAMETERS	MDL ¹	POLYSAR INTAKE	POLYSAR BIO- TREATMENT PLANT	POLYSAR 72" SEWER	POLYSAR 66" SEWER	POLYSAR 54" SEWER	POLYSAR STEREO API
Naphthalene	0.01	0.16	0.17	0.18	0.73	0.18	0.19
Acenaphthylene	0.01	-	-	-	0.012	-	-
Acenaphthene	0.01	-	-	-	-	-	0.010
Fluorene	0.01	-	-	-	-	0.034	-
Phenanthrene	0.01	0.033	0.020	-	0.039	-	-
Anthracene	0.01	-	-	-	-	-	-
Fluoranthene	0.01	-	-	-	0.016	-	-
Pyrene	0.01	-	-	-	0.014	-	-
Benzo (a) Anthracene	0.01	-	0.021	-	-	-	-
Chrysene	0.01	-	-	-	-	-	-
Benzo (b) Fluoranthene	0.02	-	-	-	-	-	-
Benzo (k) Fluoranthene	0.02	-	-	-	-	-	-
Benzo (a) Pyrene	0.02	-	-	-	-	-	-
Indeno Pyrene	0.05	-	-	-	-	0.13	-
Bibenzo (a,h) Anthracene	0.05	-	-	-	0.059	-	-
Benzo (g,h,i) Perylene	0.05	-	-	-	-	-	-

¹ MDL = Method Detection Limit; "-" Indicates not detected;

TABLE 4-19

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
PAHs (POLY AROMATIC HYDROCARBONS) (ug/l)

PARAMETERS	MDL ¹	DOW INTAKE NORTH & SOUTH PUMPHOUSE COMPOSITE	1st STREET 42" SEWER	1st STREET 48" SEWER	1st STREET 30" ACID TILE	1st STREET 54" SLUICE	2nd STREET SEWER	3rd STREET SEWER	4th STREET SEWER
Naphthalene	0.01	0.14	0.095	0.14	0.17	0.087	0.18	0.31	0.18
Acenaphthylene	0.01	-	-	-	-	-	-	0.016	-
Acenaphthene	0.01	-	-	-	-	-	-	0.010	-
Fluorene	0.01	-	-	-	0.052	0.042	0.012	0.043	0.036
Phenanthrene	0.01	0.033	-	0.012	0.046	-	0.033	0.23	-
Anthracene	0.01	-	-	-	-	-	-	0.024	-
Fluoranthene	0.01	-	-	-	0.012	-	0.014	0.012	-
Pyrene	0.01	-	-	-	-	-	0.013	-	-
Benzo (a) Anthracene	0.01	-	-	-	-	-	-	-	-
Chrysene	0.01	-	-	-	-	-	-	-	-
Benzo (b) Fluoranthene	0.02	-	-	-	-	-	-	-	-
Benzo (k) Fluoranthene	0.02	-	-	-	-	-	-	-	-
Benzo (a) Pyrene	0.02	-	-	-	-	-	-	-	-
Indeno Pyrene	0.05	-	-	-	-	-	-	-	-
Dibenzo (a,h) Anthracene	0.05	-	-	-	-	-	-	-	-
Benzo (g,h,i) Perylene	0.05	-	-	-	-	-	-	-	-

¹ MDL = Method Detection Limit; "-" Indicates not detected;

TABLE 4-20

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
PAHs (POLY AROMATIC HYDROCARBONS) (ug/l)

PARAMETERS	MDL ¹	DOW SCOTT ROAD BEFORE CARBON (NOT DISCHARGED)	DOW SCOTT ROAD AFTER CARBON	SCOTT ROAD OUTFALL	TOWNSHIP DITCH BEFORE POLYSAR
Naphthalene	0.01	4.7	0.16	0.21	0.16
Acenaphthylene	0.01	0.072	-	-	-
Acenaphthene	0.01	0.080	0.014	-	-
Fluorene	0.01	0.16	0.10	-	-
Phenanthrene	0.01	0.30	0.057	-	0.024
Anthracene	0.01	0.021	-	-	-
Fluoranthene	0.01	0.044	0.022	-	-
Pyrene	0.01	0.054	0.022	-	-
Benzo (a) Anthracene	0.01	0.014	-	-	-
Chrysene	0.01	0.023	0.014	-	-
Benzo (b) Fluoranthene	0.02	-	-	-	-
Benzo (k) Fluoranthene	0.02	-	-	-	-
Benzo (a) Pyrene	0.02	-	-	-	-
Indeno Pyrene	0.05	-	-	-	-
Dibenzo (a,h) Anthracene	0.05	-	-	-	-
Benzo (g,h,i) Perylene	0.05	-	-	-	-

¹ MDL = Method Detection Limit; "-" indicates not detected;

TABLE 4-21

MOE ST. CLAIR RIVER SURVEY

September 23-27, 1985

VOLATILE ORGANIC COMPOUNDS MEASURED IN DOW INTAKE/OUTFALLS DURING SURVEY PERIOD (ug/l)

PARAMETERS*	NORTH INTAKE	SOUTH INTAKE	1st STREET SEWER COMPLEX				2nd STREET SEWER	3rd STREET SEWER	4th STREET SEWER
			42"	48"	TILE	SLUICE			
Benzene	-	-	2	-	-	-	-	247	-
Bromoform	-	-	1	-	-	-	-	-	-
Carbontetrachloride	6	3	70	6	42	11	7	147	4
Chloroform	-	-	5	-	16	-	-	-	-
Chlorodibromoethane	-	-	7	-	-	-	-	-	-
Dichlorobromoethane	-	-	3	-	-	-	-	-	-
Dichloroethane	-	-	9	-	-	-	-	-	-
1,2-Dichloroethane	-	-	-	-	-	-	-	-	-
1,1,1-Trichloroethane	-	-	25	-	-	-	-	-	-
1,2,1-Trichloroethane	-	-	31	-	-	-	-	-	-
1,1,2,2-Tetrachloroethane	-	-	5	-	-	-	-	-	-
1,1-Dichloroethylene	-	-	5	-	120	-	-	-	-
Tetrachloroethylene	9	3	430	7	68	21	8	9	4
Trihalomethanes	-	-	16	-	16	-	-	-	-
O-xylene	-	-	-	-	-	-	-	2	-
FLOW (MGD)			14	11	4	11	12	40	77

* GC Electron Capture, not confirmed by mass spectrometer method detection limit approximately 1 ug/l

"- " Not Detected

TABLE 4-22

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
 NEW YORK STATE AMBIENT WATER QUALITY
 STANDARDS AND GUIDELINES¹
 (ug/l)

COMPOUND	STANDARD(S) OR GUIDELINE(G)	COMPOUND	STANDARDS(S) OR GUIDELINES (G)
Chloroethane	- (40) ²	Pentachloroethane	-
Vinyl Chloride	0.3 (G)	1,3-Dichlorobenzene	20 (S)
Methylene Chloride	50.0 (G)	1,4-Dichlorobenzene	30 (S)
1,1-Dichloroethene	0.07 (G)	1,2-Dichlorobenzene	4.7 (S)
1,1-Dichloroethane	50.0 (G)	Total Trichlorobenzenes	10 (S)
Trans-1,2-Dichloroethene	50.0 (G)	Total Tetrachlorobenzenes	10 (S)
Chloroform	0.2 (S)	Pentachlorobenzene	-
1,2-Dichloroethane	0.8 (S)	Hexachlorobenzene	0.02 (G)
1,1,1-Trichloroethane	50.0 (G)	Hexachloroethane	-
Carbon Tetrachloride	0.4 (G)	Hexachlorobutadiene	0.5 (S)
1,2-Dichloropropane	50.0 (G)	Octachlorostyrene	-
Trichloroethene	3.0 (G)	Total BHC	0.02 (G)
Benzene	50.0 (G)	Chlordane	-(0.06) ⁴
1,1,2-Trichloroethane	0.6 (S)	Sum of DDE, DDD, DDT	-(0.003) ⁴
Bromoform	50.0 (G)	Total PCBs	0.01 (S)
Perchloroethene	0.7 (G)	Total Chlorophenols	1.0 (S)
1,1,2,2-Tetrachloroethane	0.2 (G)	Total Phenols	1.0 (S)
Toluene	50.0 (G)	2,4-D	100.0 (S)
Chlorobenzene	20.0 (S)	2,4,5-T	35.0 (S)
Ethylbenzene	50.0 (G)	Napthalene	10.0 (S)
Acrolein	-	Acenaphthylene	-
Acrylonitrile	0.07 (G)	Acenaphthene	20.0 (S)
3-Chloropropene	-	Fluorene	50.0 (G)
1,2-Dibromoethane	-(0.02) ³	Phenanthrene	50.0 (G)
M + P-Xylene	50.0 (G)	Anthracene	50.0 (S)
O-Xylene	50.0 (G)	Fluoranthene	50.0 (G)
Styrene	50.0 (G)	Pyrene	50.0 (G)
Benzo(a) Anthracene	0.002(G)	Chrysene	0.002(G)
Benzo(a) Fluoranthene	0.002(G)	Benzo(k) Fluoranthene	0.002(G)
Benzo(a) Pyrene	0.002(G)	Indeno Pyrene	0.002(G)
Dibenzo(a,h)Anthracene	-	Benzo (g,h,i)Perylene	-

¹ For the protection of drinking water supplies.

"-" Indicates that NYS does not have a standard or guideline for this compound.

² Calculated by U.S. EPA Chicago for EPS.

³ State of Florida Drinking Water Standard.

⁴ Great Lakes Water Quality Agreement.

TABLE 4-23

ST. CLAIR RIVER SURVEY - MUNICIPAL DISCHARGES

a) Levels of Selected Trace Organics in Water Samples from Study Area (ug/l)

COMPOUND	WPCP EFFLUENT	URBAN RUNOFF					
		INDUSTRIAL CSO	RESIDENTIAL CSO		INDUSTRIAL		TOWNSHIP DITCH
		Clifford	Campbell	Cathcart	Vidal North	Vidal South	Scott Road Vidal Street
Perchloroethylene	26.0	0.100	0.50	0.100	0.050	0.090	5.00
Hexachloroethane	0.002	ND	0.001	0.001	0.003	0.010	0.420
Hexachlorobutadiene	0.001	ND	0.001	0.009	0.007	0.008	0.640
QCB	ND	ND	ND	0.001	0.002	0.002	0.830
HCB	0.003	0.001	0.005	0.003	0.010	0.017	0.015
OCS	ND	ND	ND	0.002	0.002	0.001	0.018
							0.012
							0.034
							0.003

b) Annual Loadings of Selected Trace Organics Kg/year

COMPOUND	WPCP EFFLUENT	URBAN RUNOFF	TOWNSHIP
Perchloroethylene	590.0	0.78	8.8
HCE	0.045	0.078	1.6
HCBd	0.023	0.070	9.3
QCB	-0.011	0.016	0.103
HCB	0.068	0.133	0.060
OCS	-0.011	0.016	0.008

ST. CLAIR RIVER SURVEY

a) Levels of Selected Trace Organics in Sediment Samples (ug/Kg)

COMPOUND	RESIDENTIAL		INDUSTRIAL		
	Campbell	Cathcart	Vidal North	Vidal South	Township Ditch
Perchloroethylene	41	29	5.9	-	66
HCE	36	-	ND	ND	ND
HCBd	58	-	8	25	4,300
QCB	ND	-	3.3	ND	490
HCB	710	-	32	160	1,700
OCS	100	-	9.9	ND	1,400

TABLE 4.25

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
CN TUNNEL CONVENTIONAL POLLUTANTS (mg/l)

SAMPLE LOCATION	TOTAL PHENOLS	TOTAL CHLORIDE	SOLUBLE Ca ⁺	TOTAL Ca	SOLUBLE Na ⁺	TOTAL Na	HARDNESS AS CaCO ₃	ALKALINITY AS CaCO ₃	SULPHATE	pH
Dewatering Discharge	0.028	2650	92	113	1200	1180	0.88	328	90	8.1
Piezometer 24+10 P-2	0.031	5600	124	150	2000	2000	1.09	423	0.2	7.9
Piezometer 24+10 G-1	0.008	--	21	20	385	463	0.06	265	<0.1	8.2
Piezometer 24+70 P-1	0.015	--	80	3000	882	914	0.40	3100	16	8.5

⁺Ca = Calcium, Na = Sodium

--" No Data

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
VOLATILE ORGANICS - NET LOADINGS (kg/d)

PARAMETERS ²	MDL ¹	CN TUNNEL DEWATERING DISCHARGE	CN TUNNEL PIEZOMETER 24 + 10 P-2	CN TUNNEL PIEZOMETER 24 + 10 P-1	CN TUNNEL PIEZOMETER 24 + 70 P-1
Chloroethane	2	-	-	-	NOT ANALYSED DUE TO EXCESSIVE SOLIDS
Vinyl Chloride	2	-	-	-	
Methylene Chloride	1	-	<1.0	-	
1,1-Dichloroethane	1	-	-	-	
1,1-Dichloroethane	1	<1.0	-	-	
Trans-1,2-Dichloroethane	1	1.2	-	-	
Chloroform	1	-	-	-	
1,2-Dichloroethane	1	3.3	-	<1.0	
1,1,1-Trichloroethane	1	16	-	-	
Carbon Tetrachloride	1	-	-	-	
Bromodichloromethane	1	-	-	-	
1,2-Dichloropropane	1	-	-	-	
Trichloroethene	1	<1.0	-	-	
Benzene	1	2.9	<1.0	-	
Dibromochloromethane	1	-	-	-	
1,1,1,2-Trichloroethane	1	-	-	-	
2-Chloroethyl Vinyl Ether	2	-	-	-	
Bromoform	1	-	-	-	
Tetrachloroethene*	1	7.8	<1.0	-	
1,1,2,2-Tetrachloroethane	1	-	-	<1.0	
Toluene	1	-	-	-	
Chlorobenzene	1	-	-	-	
Ethylbenzene	1	<1.0	-	-	
Acrolein	5	-	-	-	
Acrylonitrile	5	-	-	-	
3-Chloropropene	2	-	-	-	
1,2-Dibromoethane	1	-	-	-	
Meta + para xylene	1	-	-	-	
Styrene	1	-	-	-	
Ortho xylene	1	-	-	-	
Pentachloroethane	1	-	-	-	

* Perchloroethylene

1 MDL = method Detection Limit; "-" Indicates not detected; "xx" Indicates peak present below MDL;

2 Also analysed but not detected (MDL in Brackets): chloromethane (2), Bromoethane (2), CTS-1,3-or-chloropropene (2), trans-1,3-dichloropropene (2), trichlorofluoromethane (2), 1,1,2-trifluoro-1,2-trichloroethane (1), dichloroacetonitrile (5), 1-bromo-2-chloro ethane (1), bromobenzene (1), 1,1,2,3-tetrachloropropene (2).

TABLE 4.27

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
VOLATILE ORGANICS - NET LOADINGS (ug/l)

PARAMETERS ²	MDL ¹	CN TUNNEL DEWATERING DISCHARGE	CN TUNNEL PIEZOMETER 24 + 10 P-2	CN TUNNEL PIEZOMETER 24 + 10 G-1	CN TUNNEL PIEZOMETER 24 + 70 P-1
1,3-Dichlorobenzene	0.005	-	-	-	-
1,4-Dichlorobenzene	0.01	-	-	-	-
1,2-Dichlorobenzene	0.005	-	-	-	-
1,3,5-Trichlorobenzene	0.006	-	-	-	-
1,2,4-Trichlorobenzene	0.007	-	-	-	-
1,2,5-Trichlorobenzene	0.008	-	-	-	-
1,2,3,5-Tetrachlorobenzene	0.002	-	-	-	-
1,2,4,5-Tetrachlorobenzene	0.004	-	-	-	-
1,2,3,4-Tetrachlorobenzene	0.002	-	-	-	-
Pentachlorobenzene	0.001	0.0021	-	-	-
Hexachlorobenzene	0.001	0.0022	-	-	-
Hexachloroethane	0.001	-	-	-	-
Hexachlorobutadiene	0.001	0.0004	-	-	-
Octachlorostyrene	0.001	0.0005	-	-	-
X-Benzenehexachloride	0.001	0.0003	-	-	-
Linsane	0.001	-	-	-	-
8-Chlorane	0.002	-	-	-	-
P,p'-DDE	0.002	-	-	-	-
P,p'-DDD	0.002	-	-	-	-
P,p'-DDT	0.005	-	-	-	-
Mirex	0.006	-	-	-	-
Total PCB's	0.002	-	-	-	-

¹ MDL = method Detection Limit; "u" Indicates not detected;

TABLE 4.28

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
CHLOROPHENOLS AND CHLOROENOXY ACIDS (ug/l)

PARAMETERS ²	MDL ¹	CN TUNNEL DEWATERING DISCHARGE	CN TUNNEL PIEZOMETER 24 + 10 P-2	CN TUNNEL PIEZOMETER 24 + 10 G-1	CN TUNNEL PIEZOMETER 24 + 70 P-1
2,6-Dichlorophenol	0.001	-	-	-	-
2,4-Dichlorophenol	0.001	-	-	-	-
2,3-Dichlorophenol	0.001	-	-	-	-
2,4,6-Trichlorophenol	0.003	-	-	-	0.006
2,3,6-Trichlorophenol	0.001	-	-	-	-
2,4,5-Trichlorophenol	0.001	-	-	-	-
2,3,5-Trichlorophenol	0.001	-	-	-	-
3,4,5-Trichlorophenol	0.001	-	-	-	-
2,3,5,6-Tetrachlorophenol	0.001	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.001	0.0021	-	-	-
2,3,4,5-Tetrachlorophenol	0.001	0.0022	-	-	-
Pentachlorophenol	0.001	-	-	-	-
2,4-D	0.001	0.0004	-	-	-
2,4,5-T	0.001	0.0005	-	-	-

¹ MDL = method Detection Limit; "-" Indicates not detected;

TABLE 4.29

ST. CLAIR STUDY - POINT SOURCE DISCHARGES
PAHs (POLY AROMATIC HYDROCARBONS) (ug/l)

PARAMETERS ²	MDL ¹	CN TUNNEL DEWATERING DISCHARGE	CN TUNNEL PIEZOMETER 24 + 10 P-2	CN TUNNEL PIEZOMETER 24 + 10 G-1	CN TUNNEL PIEZOMETER 24 + 70 P-1
Naphthalene	0.01	0.13	0.18	0.12	1.41
Acenaphthylene	0.01	0.018	0.010	-	0.41
Acenaphthene	0.01	0.80	-	-	0.10
Fluorene	0.01	0.18	-	0.010	0.53
Phenanthrene	0.01	0.040	0.040	0.025	1.18
Anthracene	0.01	0.050	-	-	0.27
Fluoranthene	0.01	0.73	0.014	0.010	0.51
Pyrene	0.01	0.44	-	0.018	-
Benzo (a) Anthracene	0.01	0.010	-	-	-
Chrysene	0.01	-	-	-	-
Benzo (b) Fluoranthene	0.02	-	-	-	-
Benzo (k) Fluoranthene	0.02	-	-	-	-
Benzo (a) Pyrene	0.02	-	-	-	-
Indeno Pyrene	0.05	-	-	-	-
Dibenzo (a,h) Anthracene	0.05	-	-	-	-
Benzo (g,h,i) Perylene	0.05	-	-	-	-

¹ MDL = Method Detection Limit; "-" indicates not detected;

APPENDIX II

FACILITY DESCRIPTIONS

ST. CLAIR SURVEY - POINT SOURCE DISCHARGES

FACILITY DESCRIPTIONS

ESSO PETROLEUM CANADA

Products

The Sarnia Refinery of Esso Petroleum Canada (a division of Imperial Oil) processes crude oil into gasolines and fuels, petrochemical feedstocks, lubricating oils and waxes.

Wastewater Collection and Treatment

The following description applies to the refinery water systems which serve the refinery as well as the petrochemical operations noted above.

The cooling water streams are segregated from the oil-contacting water streams. Once through cooling water (OTCW) passes through four parallel API separators, before discharging to the St. Clair River, as a safeguard against upsets such as exchanger leaks.

The oil-contacting water streams are collected and treated before release. Sour waters are steam stripped of hydrogen sulphide and ammonia and biologically treated to remove phenolics before combining with other process water in the biox plant. Stormwater, tank farm runoff and process water pass through three parallel API separators before filtration through a dual-media filter. The filter effluent discharges to the refinery activated

sludge plant (biox). The final effluent combines with OTCW from two of the cooling water API separators and discharges to the river.

The intake and Biox effluent were sampled during the study.

ESSO CHEMICAL CANADA

Products

Esso Chemical Canada (ECC) manages and operates petrochemical manufacturing facilities at Sarnia. A small number of the ECC operations are integrated with the petroleum refinery operated by Esso Petroleum Canada (olefins, solvents and lubricant additives). An independent Esso Chemical plant is located east of the Esso refinery. It has its own cooling and wastewater system. These comments will apply only to the non-integrated Esso Chemical plant.

The non-integrated section of the plant manufactures polyvinylchloride (PVC) and polyethylene resins and aromatics (benzene, toluene and xylene). BTX is produced from feedstock supplied by the refinery.

Wastewater Collection and Treatment

Esso Chemical's process wastewater discharges to (in parallel) two circular oily water separators. From the separators, the combined effluent passes through two dual media filters in parallel and then through an activated carbon absorber. The

treated effluent discharges to the clean water impounding basin. Refinery biosludge is added to the filter effluent as it enters the clean water impounding basin. This results in the further removal of phenols prior to discharge to the river. When flow during heavy rain exceeds the capacity of the dual media filters and carbon adsorber system, excess water is diverted to the oily impounding basin and held until it can be brought back through the filter and carbon treaters under control. The oily water impounding basin is, therefore, a hold-up facility only. When the TOC (Total Organic Carbon) analyzer on the effluent from the Aromatics Plant shows unacceptable hydrocarbon levels, the effluent is diverted to the oily impounding basin and brought back under controlled rate. Uncontaminated once-through cooling water discharges into the clean water basin and the combined effluent discharges to the St. Clair River. The service water is obtained from the St. Clair River via the Esso Petroleum refinery.

The Esso Petroleum intake and the Esso Chemical final effluent were sampled during the study.

POLYSAR LIMITED

Products

Polysar manufactures synthetic rubbers (SBR, nitrile, BR, butyl and halobutyl) and rubber latex. It also produces some of the basic petrochemicals for use at the Sarnia site. This includes the production of ethylbenzene and styrene, and the extraction and purification of butadiene and isobutylene.

Wastewater Collection and Treatment

The major discharges from Polysar flow directly to the St. Clair River and include: the bio-treatment plant effluent, 54" sewer, 66" sewer and 72" sewer. The last section of the Township ditch from Vidal Street to the river is lined with concrete and flows through Polysar. A number of minor discharges to the ditch do originate with Polysar. The bio-treatment plant effluent and the flow from the Township ditch combine at the river and discharge via an extended diffuser outfall.

The bio-treatment plant came on line in 1983. It treats the majority of Polysar's process wastewater as well as selected wastewater from other industries which pay Polysar to treat their waste. The 54" sewer discharges boiler blowdown, cooling water and excess intake water. The 66" sewer discharges treated Styrene II and Butyl II unit wastewaters, cooling water and stormwater. The 72" sewer discharges non-contact cooling water.

The water supply for the plant is obtained from the river just downstream of the Biox/Township ditch outfall.

The intake, bio-plant effluent, 54", 66" and 72" sewers were all sampled during the study. In addition, the Stereo API oily water separator discharge was also sampled. This effluent discharges to the 66" sewer, downstream of the 66" sewer sampling location.

DOW CHEMICAL CANADA INC.

Dow Chemical operates a diversified chemical/plastics complex in Sarnia composed of a number of specific manufacturing plants. The product line includes styrene, polystyrene, propylene glycol, chlorine and caustic soda, chlorinated solvents, latices, vinyl chloride, high and low density polyethylene, epoxy resins, polyglycols and propylene oxide. It also markets a number of additional organic products manufactured by other Dow plants in Canada and the U.S.A.

Wastewater Collection and Treatment

The complex has eight discharges to the St. Clair River and two service water intakes both of which occur downstream of some of Dow effluent discharges. The sewers and their approximate flows on the date surveyed are listed below. The majority of the water used is for OTCW. Other uses are equipment washing, steam production and direct contact with products/raw materials.

Sewer Identification	Flow (November 27, 1985) 10 ⁶ L/d
1. 42" 1st Street Sewer	65
2. 48" 1st Street Sewer	56
3. 30" Tile Drain	10
4. 54" Sluice	30
5. 2nd Street Sewer	66
6. 3rd Street Sewer	120
7. 4th Street Sewer	565
8. Steam Plant Sewer (not sampled)	20 (1984 Average)

The 42" 1st Street sewer receives process wastewater and/or cooling water from the vinyl chloride monomer, solvents plants, and the propylene oxide plant (cooling water only). Gas scrubber waste from vinyl chloride production is subject to pH control. The 48" 1st Street sewer receives cooling water from the vinyl chloride monomer and solvents plants.

The 30" Acid Tile Drain receives process water and cooling water from the vinyl chloride plant. The 54" Sluice receives the bulk of process and cooling water from the propylene oxide, brine treatment, chlorine and caustic plants. The 2nd Street sewer receives laboratory wastes, polystyrene process effluent which has been treated by a phase separation separator, polystyrene cooling water, and process water and cooling water from the propylene oxide derivatives plant. Process wastewater from the propylene oxide plant discharges to the biological treatment plant.

The 3rd Street sewer receives process and cooling water from the styrene (oil separator), latex (coagulation and phase separation) and high density polyethylene (solids separators) plants.

The 4th Street sewer receives the biological treatment plant effluent and process and cooling water from the chlor-alkali I plant. In addition, process and cooling water from the low density polyethylene, epoxy resin and styrene plants also discharge to this sewer.

All sewers and intakes, except for the steam plant discharge, were sampled during the study.

SUNCOR SUNOCO GROUP

Products

The Sunoco Refinery converts crude oil from western Canada into gasolines, kerosene, heating oils, heavy fuel oils, aromatics such as benzene, xylene and toluene, and light hydrocarbon gases and liquids.

Wastewater Collection and Treatment

Sour process waters are stripped to remove hydrogen sulphide and ammonia. Spent caustic is neutralized. The effluent from these treatment processes combines with other oily process water and passes through an API separator to remove oil. Following equalization, induced air floatation (IAF) is applied to remove fine oil droplets suspended in the effluent. The effluent is treated biologically in an aeration basin to remove phenolics and other biodegradable compounds. Following final clarification, the effluent discharges to an impounding basin.

Contaminated stormwater is collected and treated for oil removal through an API separator followed by induced air floatation before discharging to the impounding basin. The impounding basin overflow combines with once through cooling water (OTCW), which has passed through an API separator, and discharges via a single outfall to the river. In the case of an upset, the impounding basin contents can be recycled through the process treatment system, entering at the equalization basins. The water supply is collected from the river at Suncor's product loading dock, which is downstream of Dow Chemical.

The River was sampled from above the intake and the impounding basin effluent was also sampled during the study.

City of Sarnia WPCP

The Sarnia sewage treatment plant employs primary treatment with phosphorus removal and has a design capacity of 68.2×10^6 L/d. The final effluent discharges to the river just south of Esso. This effluent was sampled during the study.

Township Ditch

The Township ditch carries runoff from an area south of Sarnia's residential and business core. The drainage system is bounded approximately by the CNR railway track south of Confederation Street on the north, Modeland Road on the east, Churchill Road on the south and the St. Clair River on the west. It receives stormwater runoff from undeveloped and developed land, waste disposal and product storage areas, treated and untreated runoff and industrial effluent and cooling water.

The first major upstream area of influence is the Scott Road ditch which serves an industrial waste disposal area (Scott Road landfill). Waste disposal sites along Scott Road are owned by Polysar, Dow Chemical, Fiberglass, Imperial Oil Enterprises (Refinery and Chemical Plant) as well as the City of Sarnia (sewage sludge disposal lagoons). The Scott Road ditch runs along the western edge of the industrial wastes disposal area and receives treated leachate and/or untreated storm runoff before joining the Township ditch, which up to this point contains

mostly undeveloped area runoff. An open ditch exists along Scott Road from Churchill Road to Imperial Avenue and from there, a submerged tile conveys runoff to the Township ditch. The Imperial Enterprises waste disposal site located north of Churchill Road is capped and surface runoff discharges to the ditch.

The Fiberglass disposal site is north of Imperial's and contains buried waste fiberglass. Bonding resins and dyes were at one time leaching out of this site. The leachate was collected and pumped into a holding lagoon where it was treated with calcium chloride before discharging to the Scott Road tile drain. The site was subsequently capped and a leachate collection system was installed. Leachate is now shipped off property for treatment and disposal, however, there are occasional breakouts when leachate escapes into the ditch.

The Dow Chemical disposal site is located directly north of Fiberglass. A reinforced steel barrier composed of interlocking steel pilings retains all leachate within the disposal site (pilings down to unfractured clay bed at 3 to 4 meters). The leachate is collected in a perimeter pond at the north edge of the property and pumped through carbon filters before being discharged to the Scott Road ditch. This discharge is intermittent and depends on precipitation and the level of leachate in the pond. Leachate from the Dow disposal site, prior to the installation of the carbon filters contaminated the sediments of the Scott Road ditch and the Township ditch, with hexachlorobenzene (HCB) and hexachlorobutadiene. The Scott Road ditch was subsequently excavated and replaced with a submerged corrugated steel sewer. In 1983/84 Dow dredged the affected section of the

Township ditch and disposed of the sediment at the company landfill site.

The Polysar disposal site is located south and east of the Dow site. The leachate is aerated and then directed to a fly ash pond which acts as a filter/absorbant. Storm runoff and treated leachate from the fly ash pond discharges periodically to the Scott Road ditch.

Holmes Insulation Limited is located on Scott Road and discharges cooling water only to the Scott Road ditch opposite the Esso Petroleum disposal site. Pipe insulation, insulating block, board, felts, blankets and cements, bulk and blowing wool are manufactured on-site. Process water is entirely recycled.

Upstream of the point at which it joins the Scott Road ditch, the Township ditch receives surface runoff from the areas of Plant and Indian Roads and the MacGregor Side Road. The CN yard runoff passes through an oil-water separator and also discharges to this part of the ditch.

Moving further downstream, there are inputs to the ditch from Esso Chemical (stormwater), Cabot Carbon, Fiberglass (factory) and Polysar. Cabot Carbon manufactures carbon black from liquid feedstock and natural gas. Cooling tower blowdown, laboratory wastes, boiler blowdown, equipment wash water and surface runoff discharge to the Township ditch. A wastewater treatment system is now being installed to remove carbon black and oil from the effluent. Fiberglass manufactures glass fiber insulation with phenolic and urea resins incorporated into the product. Process water passes through a solids separator before combining with cooling water and discharging to the ditch. The

process water contains minute beaded glass and would not normally be contaminated by resins unless a spill occurred within the plant.

The final section of the Township ditch is lined with concrete and flows through Polysar property. At the river it combines with the Polysar biotreatment effluent and discharges via a submerged diffuser.

During the study, the Dow landfill leachate treatment system was assessed (samples collected before and after carbon treatment). The Scott Road outfall was also sampled by EPS and NWRI. The Township ditch was sampled just upstream of Polysar on the west side of Vidal Street at the Armak Chemicals Building entrance by EPS and east of Vidal Street by NWRI. Both water and sediment were collected at the latter locations.

APPENDIX III

SAMPLING AND ANALYTICAL METHODS

SAMPLING METHODS

The majority of samples collected were grabs. Stainless steel containers were used to collect the sample which was then poured into the various sample bottles (1 L amber glass for extractable organics, 60 mL amber glass for volatile organics).

The stainless steel containers were prepared by solvent rinsing, repeated distilled water rinse and heat treated. The container was then covered with solvent/distilled water rinsed aluminum foil. The 1 L amber glass bottles were new bottles only which had been acid washed, distilled water rinsed and heat treated. The 60 mL amber glass bottles were detergent washed, rinsed with tap and distilled water and dried at 105°C. Sodium thiosulphate was added to remove free chlorine from the samples. All bottles had screw on caps with Teflon lined septa.

At locations where 3 grab samples were collected, the individual samples were composited by the laboratory. The extractables samples were combined prior to extraction. The volatiles were combined by piercing the septum with a narrow bore hypodermic needle and withdrawing equal aliquots from each grab sample. The composite sample was then injected into the purge vessel.

Twenty-four hour composite samples were collected using Horizon interval samplers (not-flow proportioned) which sampled continuously for approximately 5 minutes of each quarter hour. Sample was conveyed to the peristaltic pump using Teflon tubing and a short section of silicone in the pump head. Teflon was also used to convey the sample to a glass 18 L carboy which had

been prepared in the same manner as the stainless steel containers.

Analytical Methods

The analytical methods are briefly stated below. The reference or individual noted with each method should be consulted for the details.

1. Volatile Organics

U.S. EPA method 624

Federal Register October 26, 1984

Part VIII Environmental Protection Agency

40 CFR Part 136

2. Chlorinated Neutral Extractables

Dr. Barry Oliver, NWRI Burlington

1-416-336-4604

Method involves liquid liquid extraction at pH 2 with hexane (hexane/acetone for sediments). Following clean-up, extracts run by dual capillary column GC with electron capture (EC) detector.

3. Chlorophenols and Chlorophenoxy Acids

Dr. Mike Fox, NWRI, Burlington

1-416-336-4604

Method involves liquid liquid extraction at pH 2 with hexane. Sample extract is methylated with diazomethane. Sediment was back extracted into an aqueous base and

re-extracted. Analysed by dual capillary column GC-EC (packings Hewlett Packard Ultra 2 and OV17).

4. PAHs

Dr. Bill Lee, NWRI, Burlington
1-416-336-4645

Method involves 3 extractions with methylene chloride. The extract is evaporated and hexane was added. The extract was cleaned up using an activated silica gel column. The first fraction was eluted with 50 mL of hexane and was discarded. The PAH fraction was then eluted with 50 mL of 40% methylene chloride and 60% hexane. The extract was again evaporated down and brought up to 1 mL with toluene. The analytical method was GC/MS capillary column, U.S. EPA Method 625 (from Federal Register - see Volatiles Section).

5. Chlorinated Dibenzo-p-dioxins

Dr. Frank Onuska, NWRI, Burlington
1-416-336-4635

Liquid liquid extraction, carbon fiber clean-up, high resolution GC and high resolution MS. Two column types were used, one for isomer specific tetrachlorodibenzo-p-dioxins and the second for the remaining chlorinated dioxins. The detection limit for these compounds in sediment was approximately 0.003 ug/kg.



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